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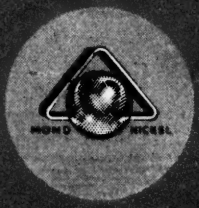

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INDEX

Nickel Page

Use of High-Purity Nickel for Electron-Tube Cathodes 105
Chemisorption of Gases on Vacuum-Deposited Nickel 105
Transport Phenomena with Iron and Nickel 106

Electrodeposition and Other Coating Methods

History of Electroless Plating 106
Chemistry of Electroless Nickel Plating 106
Properties of Chemically-Deposited Nickel 107
Electroless Nickel Plating: Solution Compositions and Plating Conditions 107
Advantages and Limitations of Electroless Nickel Plating 107
Applications of Electroless Nickel Plating 107
Test Methods Relevant to Chemically-Deposited Nickel and Electroless-Nickel-Plating Solutions 107
U.S. Patents Relevant to Electroless Nickel Plating 108
Bibliography on Electroless Nickel Plating 108
Recrystallization of a Molybdenum-Titanium Alloy: Influence of Nickel Plating 108

Non-Ferrous Alloys

Lattice Parameters of Copper-Zinc-Nickel α Solid Solutions 108
Hot Extrusion of Non-Ferrous Metals 108

Constructional Steels

Super-Duty Steels 109
Quality Requirements in Aircraft Engines 109
Application of Steel to Aircraft Structures 109
Factors Influencing the Ductility and Fatigue-Resistance of Low-Alloy Nickel-Chromium-Molybdenum Steel Forgings 109
Relationship between Inclusions and Rolling Fatigue in Ball Bearings 110
Quality Control in the Production of Nickel-Chromium-Molybdenum Steel 110
Control of Segregation and Ingot Structure in Nickel-Chromium-Molybdenum High-Strength Steel 111
Vacuum De-gassing of Nickel-containing Forging Steels 111
Vacuum Melting of Steels 111
Vacuum Induction Melting of Low-Alloy Steels 111
Steel for Aeronautical Applications: Quality Requirements 111
Influence of Nickel and Manganese on the Impact-Resistance of Medium-Carbon Cast Steels 112
Use of Nickel-Chromium-Molybdenum Steel in the Construction of the Bathyscaphe 112
Check-Analysis Limits for Wrought Low-Alloy Steels 112

Heat- and Corrosion-Resisting Materials

Requirements of 'Reactor-Grade' Materials 113
Stainless and Hot-Work Die Steels for High-Strength Applications 113
Effects of Radiation on Stainless Steels 113
Analysis Control of '17-7 P.H.' Stainless Steel 113
Hot-Working of Iron-, Cobalt- and Nickel-base Materials 114
Intergranular Cavitation, Structure and Creep of 'Nimonic 80A' 114

Page

Sigma Phase in the Chromium-Iron and Chromium-Nickel Systems 115
Suitability of 'Inconel' for Nuclear-Power Applications 115
Oxidation of Heat-Resisting Steels in the Presence of Alkali-Sulphate Combustion Products and Sulphur (VI) Oxide 116
Oxidation of Nickel-containing Materials in Carbon Dioxide at High Temperatures and Pressures 117
Corrosion Products of Nickel and Nickel Alloys: Bibliography 118
Relationship between the Velocity of a Corrosive Environment and the Corrosion Behaviour of Metals 118
Corrosion of Steels in Marine Tropical Environments 118
Mechanism of Stress Corrosion 119
Effect of Electric Strain on the Electrode Potential of Metals 119
Surface Structure and Chemical Interaction 119
Effect of Stress on the Corrosion Failure of γ-Phase Uranium Alloys 119
Crack Propagation During Stress Corrosion 119
Stress Corrosion of α-Brass and Similar Alloys 119
Application of Electron Microscopy to Study of Stress Corrosion 120
Rôle of Corrosion Products in Stress-Corrosion Cracking of Austenitic Steel 120
Relationship between Microtopology of the Corrosion Product and Stress-Corrosion Failure 120
Stress Corrosion of Single Crystals of Stainless Steel 121
Development and Path of Stress-Corrosion Cracks in Austenitic Stainless Steels 121
Influence of Temperature on Stress Corrosion of Stainless Steels in Chloride Waters 122
Stress Corrosion of Austenitic Stainless Steel by Hot Salts 123
Influence of Nickel Content on Stress Corrosion of Alloys and Steels 123
Effect of Neutron Irradiation on Susceptibility of Austenitic Stainless Steel to Stress Corrosion 124
Influence of Age Hardening on the Susceptibility of a Copper-Nickel-Silicon Alloy to Stress Corrosion 124
Corrosion of Ancient Bronze 125
Stress-Corrosion Cracking of Low-Carbon Steel 125
Cracking of Steel under Stress in the Presence of Hydrogen 125
Stress-Corrosion Cracking of Mild Steel 125
Current Approaches to the Problem of Stress Corrosion 125
Anodic-Passivation Studies of Stainless Steels 125
Application of Anodic Protection in the Chemical Industry 126
Anodic Protection of Stainless-Steel Equipment in a Sulphonation Plant 127
Potentiostatic Isolation of Microstructural Phases in Nickel Alloys 127
Corrosion-Resistance and Weldability of Chromium-Manganese-Nickel Austenitic Stainless Steels 128
Corrosion Tests on a Sintered Nickel-Iron-Molybdenum Alloy 128
Heat-Treatment of Stainless Steels 129
Consumable-Electrode-Melted Corrosion- and Heat-Resistant Steel 129

Analysis 129

ABSTRACTS OF CURRENT PUBLISHED INFORMATION ON NICKEL AND ITS ALLOYS

NICKEL

Use of High-Purity Nickel for Electron-Tube Cathodes

K. M. OLSEN: 'High-Purity Nickel.'

Bell Laboratories Record, 1960, vol. 38, Feb., pp. 54–8.

Studies at the Bell Laboratories have shown that the level of electron emission associated with a specific oxide-coated nickel cathode, and the time for which a given emission level can be maintained, are governed to a great extent by the impurities present in the basis nickel. Attempts to determine the effects of individual impurities have not met with success, due mainly to the difficulty of studying a given addition without interference from other contaminants introduced viâ the raw materials or during the melting process. In the past, the suitability of a given melt of commercial nickel for a particular cathode application could, therefore, be determined only on an empirical basis, i.e., by vacuum-tube life tests. This procedure does not, however, satisfy the requirements of vacuum tubes of new design. Work on submarine-cable tubes designed to have long life, and to operate at higher frequencies and greater bandwidths than those at present in transoceanic service, has emphasized the need for cathode nickel of closely controlled impurity content. The present paper summarizes investigations which have culminated in the production of over 1500 lb. of high-purity nickel (containing controlled additions of desired elements) suitable for use both in fundamental research and in development work on the new submarine-cable tube.

A survey revealed that the purest nickel commercially available was that produced, in the form of powder, by The Mond Nickel Company, Ltd. The relatively high carbon and oxygen contents of the powder (0·07 and 0·02 per cent., respectively) gave rise to difficulties at first, but subsequent work resulted in the development of a procedure by which sound ingots were produced from such powder. This procedure is summarized as follows:

'The nickel powder was sintered, to form nickel slugs, by a wet-hydrogen treatment at a low temperature for a long period of time. This step, carried out at 800°C. for 16 hours, reduced the oxygen content and lowered the carbon from about 0·07 per cent. to about 0·007 per cent. The sintered slugs were then melted down in dry hydrogen in the controlled-atmosphere furnace. During melting, a steady flow of hydrogen was maintained at 20 cu. ft. (0·56 m.^{3}) per hour. After a 10-minute period to allow the molten charge to reach a stable temperature of about 1500°C., the dry hydrogen was purged from the furnace with dry helium, and all gases were removed by evacuation. Next, dry hydrogen was reintroduced for 15 minutes, to effect a further reduction of the small residual quantities of carbon and oxygen in the melt, and the hydrogen was then purged again with helium and subsequent evacuation. Helium was then reintroduced to establish a flow of 20 cu. ft. per hour at a pressure of one atmosphere.

'If high-purity nickel with no addition is desired, the molten charge is at this point poured into an alundum-coated steel mould. Careful processing into strips will provide a nickel of exceptional purity (*comparative data on commercial grades of cathode nickel illustrate the marked decrease in impurity content*). The purity is such that no single element is present in amounts exceeding 50 parts per million (0·005 per cent. by weight).

'On the other hand, if nickel containing other elements is desired, the additions are made at this time, using a hopper device actuated by external controls. After allowing 3 to 5 minutes for complete solution of the added elements, the molten charge is poured into the ingot mold. Ingots produced in this manner weigh 26 lb. (11·5 kg.) and are 1½ in. (3·75 cm.) thick.

'Careful processing controls and good housekeeping practices are required to avoid contamination during fabrication of the ingot into strip. The ingots were hot rolled in air at 1000°C. to a thickness of ½ in. (1·25 cm.), and the surfaces were then machined to remove the oxide scale. Cold rolling was employed to reduce the thickness further to 0·08 in. (2 mm.). The strip was then annealed at 800°C. in hydrogen. After annealing, the strip was cold rolled to 0·020 in. (0·5 mm.), annealed again, and finally rolled to finished strip having a thickness of 0·003 in. (0·075 mm.). A clean 'Inconel' tube was used for the annealing treatments. Special rolls were reserved for rolling, and pure kerosene was used as a lubricant during rolling, to minimize contamination from this source. Lubricants and other surface contaminants were carefully removed prior to each anneal.'

Corrosion Products of Nickel: Bibliography

See abstract on p. 117.

Chemisorption of Gases on Vacuum-Deposited Nickel

R. SUHRMANN and G. WEDLER: 'Electronic Interaction as a Preliminary Stage to Chemical Reactions between Metals and Chemisorbed Gases.'

Zeitsch. Elektrochemie, 1959, vol. 63, Oct., pp. 748–56; disc., p. 757.

Study of variations in the electrical resistance and photoelectric sensitivity of thin metal films deposited under an ultra-high vacuum provides, during chemisorption of gases, a means of determining their state of bonding. The bond between the chemisorbed molecule and substrate resembles that of a chemical surface compound. The strength of the bond can vary considerably.

During chemisorption, carbon monoxide is bonded to nickel predominantly by the surface dipole with the negative pole directed outwards, while simultaneously metal electrons are severely stressed in the direction of the molecule. In the case of copper, on the other hand, an increase in the electron concentration between both partners occurs at low temperatures, conjointly with a strong displacement of metal electrons in the direction of the molecule, and of molecule electrons in the direction of the metal; the simultaneous presence of two types of bond are postulated for bismuth.

Nitrogen is chemisorbed on nickel only at low temperatures, and in a similar way to carbon monoxide on copper; stressing of the metal electrons is, however, weaker. In the case of tungsten, a weak dissociation of the nitrogen occurs at 293°K. and leads to a bond with the negative pole directed outwards.

At 90°K., oxygen also dissociates on nickel and tungsten, to atoms which, under the severe stress of metal electrons, are bonded by the surface dipole with its negative pole directed outwards. The oxygen atoms act as electron recipients also in the case of bismuth; simultaneous adsorption of molecular oxygen is also observed, which decreases the potential of the electron as it emerges from the bismuth surface.

Adsorption of hydrogen on bismuth is very small and probably molecular. On the *d*-metals, nickel and platinum, molecular and atomic hydrogen are simultaneously present. The latter can become chemisorbed as H^- or can dissociate into proton and electron, during which it can penetrate into the surface film at a rate which is higher with platinum than with nickel.

Transport Phenomena with Iron and Nickel

H. SCHAEFER and K. ETZEL: 'The Transport of Iron and Nickel by the Reaction $Me + 2\ HCl = MeCl_2\,(g) + H_2$, and the Stability of the Gaseous Sub-chlorides FeCl and NiCl.'

Zeitsch. anorganische Chemie, 1959, vol. 301, Sept., pp. 137-53.

Quartz tubes containing Fe and $FeCl_2$ (or Ni and $NiCl_2$) were exposed to a temperature gradient, such that the metal was, for example, subjected to a temperature of 900°C., and the dichloride to one of 600°C. In the presence of even trace amounts of HCl, H_2 or H_2O the metal migrated to the colder zone, where it was deposited, in the form of a mirror or crystals, according to the reversible reactions:

$$Fe + 2\,HCl \rightleftharpoons FeCl_2\,(g) + H_2 \text{ or}$$
$$Ni + 2\,HCl \rightleftharpoons NiCl_2\,(g) + H_2$$

In the absence of hydrogen compounds, however, no further metal transport occurred. The equations

$$Fe + FeCl_2\,(g) \rightleftharpoons 2\,FeCl(g) \text{ and}$$
$$Ni + NiCl_2\,(g) \rightleftharpoons 2\,NiCl(g)$$

were not therefore involved in the transport. On the basis of this finding, the limiting values were determined for the enthalpies of formation of the monochlorides FeCl and NiCl derived from the spectrum.

The virtually complete removal of hydrogen necessary to the transport experiments could not be achieved by heating in a high vacuum. The hydrogen was, however, successfully removed when nickel chloride was sublimed over the metal at a temperature of 1000°C.

ELECTRODEPOSITION AND OTHER COATING METHODS

Electroless Nickel Plating: Symposium

AMER. SOC. TESTING MATERIALS: 'Symposium on Electroless Nickel Plating (Catalytic Deposition of Nickel-Phosphorus Alloys by Chemical Reduction in Aqueous Solution).'

A.S.T.M. Special Tech. Publication No. 265, 1959; 67 pp.

The information presented in this Symposium was compiled as a result of the formation, under the aegis of A.S.T.M. Committee B-8 on Electrodeposited Metallic Coatings, of a task group which was to investigate the desirability of publishing a specification covering electroless nickel plating. It became apparent that a survey of the current state of knowledge in the field was a prerequisite to any work on specifications, and Section C of Subcommittee I was formed to make the survey. The information collected evoked such interest that it has now been made generally available in the form of this Symposium.

The scope of the nine papers comprising the Symposium is indicated briefly below.

History of Electroless Plating

A. BRENNER: 'History of the Electroless-Plating Process', pp. 1-2.

Historical review of the electroless nickel-plating process, embracing the early studies of the reducing power of the hypophosphites, the accidental discovery of electroless nickel plating by Brenner and Riddell in 1944, and the subsequent commercial development of the process.

Chemistry of Electroless Nickel Plating

G. GUTZEIT: 'Chemical Reactions', pp. 3-12.

The author's survey of the chemical reactions involved in electroless nickel plating includes notes on reaction kinetics, the mechanism of the fundamental reactions, and factors affecting the life and stability of the plating solution (See also the comprehensive review by the same author to which reference was made in *Nickel Bulletin*, 1960, vol. 33, No. 4, p. 70.)

Properties of Chemically-Deposited Nicke

W. H. METZGER: 'Characteristics of Deposits', pp. 13–20.

The author summarizes data available in the literature on the properties of chemically-deposited nickel (i.e., nickel-phosphorus-alloy coatings ranging in phosphorus content from 6 to 10 per cent.).

The data presented are commented upon in sections relating to the following factors: composition, appearance, structure, hardness, strength and ductility, density, electrical and magnetic properties, resistance to attack by reagents (the data tabulated cover a wide range of industrially important reagents), and resistance to atmospheric corrosion.

Electroless Nickel Plating: Solution Compositions and Plating Conditions

A. KRIEG: 'Processing Procedures', pp. 21–37.

The paper was written with the aim of providing a résumé of the experience gained in the field of electroless nickel plating since the development of the process in 1947. The author's review is supplemented and illustrated by numerous data culled from the literature.

In the first section of the paper the two types of plating solution (alkaline and acid) in general commercial use are discussed in relation to their composition, their advantages and limitations, ease of control, and rates of deposition. Contamination and purification of the solution are then considered, and the causes, effects and avoidance of spontaneous decomposition are discussed. Information is given also on the use of brighteners and methods of solution control.

The second section, concerned with plating conditions, covers the effects of temperature and solution agitation.

Equipment and materials of construction, the subjects of the third section, are considered in terms of batch plating and such continuous-plating techniques as the 'Lustralloy', 'Kanigen', and 'Alcoplate' processes.

In the last three sections of the review the author notes the non-metallic and metallic materials reported in the literature to have been nickel plated by electroless processes, outlines the pre-plating procedures which experience has shown to give satisfactory results for various basis materials, and finally summarizes the information available on post-plating treatments (i.e., stripping, surface finishing, soldering and welding, heat-treatment).

Advantages and Limitations of Electroless Nickel Plating

E. B. SAUBESTRE: 'Advantages and Limitations', pp. 38–40.

The author assesses the advantages and limitations of electroless nickel plating in terms of such factors as the make-up and maintenance of the solution, the equipment necessary, the plating characteristics of the solution, and the properties of the deposits.

Applications of Electroless Nickel Plating

W. H. SAFRANEK: 'Applications', pp. 41–9.

This account of the applications found by electrolessly-deposited nickel coatings is based both on a survey of the literature and on the replies received to questionnaires circulated to about twenty American companies equipped with facilities for electroless nickel plating.

Although such plating is employed chiefly as a means of conferring corrosion-resistance on the basis metal, other properties also are important in many applications. Resistance to wear, to abrasion, and to friction and galling are factors which frequently loom large in determining the suitability of a particular type of plated coating: the lubricity of electroless-nickel-plated surfaces contributes to the prevention of wear, galling and fretting, especially in the case of components sliding against each other. The satisfactory fatigue characteristics of steel plated with nickel by chemical-reduction techniques have moreover widened the range of applications to include parts subjected to dynamic loading, and, in another field, electrolessly-deposited nickel coatings are claimed to inhibit stress corrosion of stainless steel. They are used to join dissimilar chromium alloys and dissimilar aluminium alloys, to facilitate the joining of ceramics to metals, to improve the solderability of steel and stainless steel, to salvage mismachined or worn parts, to improve the adherence of enamel to steel, to metallize plastics and ceramics, and to facilitate electrodeposition of silver and other coatings on titanium alloys. Bellows and other parts have been fabricated by electrolessly depositing a coating of nickel upon an aluminium mandrel and dissolving out the aluminium. Finally electroless nickel offers advantages over electrodeposited nickel when a uniform coating thickness is required and when corrosion protection cannot be conferred on recessed areas of interior surfaces by conventional electroplating procedures.

These and other applications are discussed by the author. Particular emphasis is placed on applications requiring corrosion-resistance and those in which resistance to wear, abrasion, friction and galling is an important factor: data are tabulated on deposit thickness and pre-plating and post-plating treatments associated with components representative of these types of application. A note on the costs of electroless nickel plating is included in the paper.

Test Methods Relevant to Chemically-Deposited Nickel and Electroless-Nickel-Plating Solutions

B. COHEN: 'Test Methods for Electroless Nickel Coating and Plating Solutions', pp. 50–2.

Methods of analyzing electroless-nickel-plating solutions and of determining the properties of chemically-deposited nickel are discussed.

Analytical procedures are outlined in an appendix to the paper.

U.S. Patents Relevant to Electroless Nickel Plating

G. GUTZEIT: 'The Patent Situation', pp. 53–62.

The author lists the U.S. patents relevant to electroless nickel plating which have been issued up to Aug. 1, 1959. The principal allowed claims of each are noted.

Bibliography on Electroless Nickel Plating

C. F. WAITE: 'Bibliography of References on Electroless Nickel Plating', pp. 63–7.

The *bibliography* contains references to 136 items of literature.

Recrystallization of a Molybdenum-Titanium Alloy: Influence of Nickel Plating

G. D. OXX: 'Recrystallization of Molybdenum-½pc Titanium Alloy by Chromium and Nickel Coatings.' *Metallurgical Society Conferences*, 1959, vol. 2, pp. 211–23; disc., pp. 223–5.
Published by Interscience Publishers, Inc., New York; Interscience Publishers, Ltd., London.

In the search for coatings which would protect molybdenum against oxidation at high temperatures, chromium, nickel, nickel-base alloys, and combinations of these materials have received considerable attention. One of the principal drawbacks to the use of nickel as a coating for molybdenum becomes evident when diffusion is permitted to occur between the coating and the basis metal. Two effects result from annealing a molybdenum-½ per cent. titanium alloy at a temperature several hundred degrees below its recrystallization temperature: (1) the molybdenum recrystallizes to a considerable depth beneath the coating, (2) a layer of nickel-molybdenum compound or compounds builds up at the nickel/molybdenum-alloy interface. Both of these effects are undesirable: the recrystallized molybdenum is weak at high temperatures and tends to be brittle at low temperatures; the compound layer is always brittle and promotes poor adherence of the coating. The investigation now reported was carried out to determine the effects, on the microstructure and mechanical properties of molybdenum-titanium alloys (containing 0·5 per cent. titanium), of the presence of nickel or chromium electrodeposited coatings.

Tensile bars 0·16 in. (4 mm.) in diameter were machined from a swaged round and stress relieved in hydrogen for one hour at 1800°F. (980°C.). Before tensile testing, the bars were subjected to one of the following treatments: chromium or nickel plated +72 hours at 2100°F. (1150°C.) in dry hydrogen; 72 hours at 2100°F. in dry hydrogen + nickel plating + 1 hour at 1600°F. (870°C.) in dry hydrogen; 72 hours at 2100°F. in dry hydrogen.

Tensile tests were carried out at temperatures up to 2200°F. (1205°C.), and specimens were subjected to metallographic examination. The results of this phase of the study showed that:

'(1) After 72 hours at 2100°F. the molybdenum directly beneath the heavy nickel plate was recrystallized to a depth of about 0·050 in. (1·25 mm.) from the Ni/Mo interface.

'(2) For short annealing times, molybdenum that was very heavily cold worked at room temperature showed a subsurface recrystallized zone (i.e., there was an apparent layer of cold-worked molybdenum between the recrystallized zone and the nickel plate) beneath electrodeposited nickel.

'(3) After a 72-hr. anneal at 2100°F., the molybdenum showed a subsurface recrystallized zone beneath an area where a very thin layer of nickel had appeared to accumulate by vapour deposition.'

Annealing of chromium-plated molybdenum for 72 hr. at 2100°F. caused the formation of a subsurface recrystallized zone beneath the chromium.

On the assumption that the recrystallization zone occurred as a result of the loss of an element which had contributed to the previously high recrystallization temperature of the alloy, an attempt was made, in the subsequent phase of the study, to determine whether diffusion of carbon (the alloy contained 0·02 wt. per cent. of carbon) or titanium was the esponsible factor. Nickel-base alloys containing ½ per cent. titanium and/or 0·3 per cent. carbon were coupled with specimens of the molybdenum alloy and annealed in dry hydrogen for 72 hours at 2100°F. (1150°C.). Extensive recrystallization occurred only in the molybdenum alloy coupled with the carbon-free nickel alloy. It is therefore concluded that addition of carbon to the protective coating offers a means of inhibiting or minimizing recrystallization in the molybdenum alloy.

NON-FERROUS ALLOYS

Lattice Parameters of Copper-Zinc-Nickel α Solid Solutions

G. A. CHADWICK amd B. B. ARGENT: 'The Lattice Parameters of the Alpha Solid Solutions of Copper-Zinc-Nickel and Copper-Zinc-Manganese.'
Jnl. Inst. Metals, 1960, vol. 88, Mar., pp. 318–9.

The work reported was initiated to study the influence of the transition metals nickel and manganese on the properties of α solid-solution brasses.

From the data tabulated it is shown that the solution of zinc and nickel alters the lattice parameter of copper to a degree slightly less than that which would result from the sum of the changes associated with the individual solutes. Zinc and manganese together expand the copper lattice to a greater extent than the sum of the expansions due to each of the solutes considered separately. These findings might, it is considered, be explicable in terms of variations in the degree of order present in the systems.

Hot Extrusion of Non-Ferrous Metals

R. CHADWICK: 'The Hot Extrusion of Non-Ferrous Metals.'
Metallurgical Reviews, 1959, vol. 4, No. 15, pp. 189–255.

The review is based on a *bibliography* of 120 items.

Some idea of its scope may be obtained from the heads under which the various facets of the subject; are surveyed: historical note; extrusion methods. extrusion tools; flow in direct extrusion; fully lubricated extrusion; inverted extrusion; surfaces of extruded products; copper and copper alloys; lead and lead alloys; aluminium and aluminium alloys; magnesium and magnesium alloys; zinc and zinc alloys; nickel and nickel alloys; titanium and titanium alloys; zirconium, molybdenum, vanadium, uranium, and beryllium; extrusion textures; and extrusion of powders.

Photomacrographs and photomicrographs supplement the textual information, and throughout the review frequent reference is made to supporting tabular data.

Potentiostatic Isolation of Microstructural Phases in Nickel Alloys

See abstract on p. 127.

CONSTRUCTIONAL STEELS

Quality Requirements of Super-Duty Steels: Symposium

AMER. INST. MINING, METALLURGICAL AND PETROLEUM ENGINEERS: 'Quality Requirements of Super-Duty Steels.'

Metallurgical Soc. Conferences, 1959, vol. 3; 309 pp. Published by Interscience Publishers, Inc., New York; Interscience Publishers, Ltd., London.
Price, $8·50; 64/-.

This volume contains the proceedings of the Technical Conference held, under the aegis of the American Institute of Mining, Metallurgical and Petroleum Engineers, at Pittsburgh, May 1958.

In defining the term 'Super-Duty Steels' the Programme Committee decided that it 'should include steels which have to resist unusual and severe environments, or which have chemical, mechanical, and physical properties that are much superior to those of conventional carbon steels. Thus, the steels used in many exotic applications are included, e.g., most stainless steels, high-strength alloy and carbon steels, and steels for meeting high-temperature or low-temperature service. After a little consideration, it appears that any steel having a non-traditional application could be included.' Many of the papers contained in the volume therefore relate mainly to constructional steels; others are, however, concerned exclusively with steels of high-alloy content. In here indicating the scope of the Conference, an attempt has been made to classify the papers on the basis of their predominant subject matter. *Accordingly, those which relate principally to low-alloy structural steels, or which are of general interest, are referred to in the following columns, while abstracts of those covering stainless and high-alloy steels will be found in the relevant section of this issue, pp.* 113–4.

Reference is made to all the papers presented at the Conference, but considerations of space preclude any but a brief outline of their scope.

Super-Duty Steels

G. A. ROBERTS: 'Super-Duty Steels and the Conference', pp. 3–5.

Introductory paper.

Equality Requirements in Aircraft Engines

M. E. CIESLICKI: 'Aircraft Engines', pp. 7–4; disc., pp. 14–15.

The author discusses the problems associated with the development of aircraft engines (particularly jet engines) in the light of weight considerations, variations in the properties of the materials of construction, and the need for high-quality materials.

Application of Steel to Aircraft Structures

F. R. KOSTOCH: 'The Application of Steel to Airframe Structures', pp. 17–23; disc., pp. 23–31.

In this paper, which comprises a general survey of the operational conditions to which steels are exposed in airframe applications and of the properties required, the author's aim is 'to show why and how steels will be used, the problems which will arise from their use, and, most importantly, what the steel industry must do to support the airframe industry'.

Design selection of materials and fabrication prerequisites are considered, and the paper ends with a résumé of the service conditions and property requirements associated with airframe applications.

Factors Influencing the Ductility and Fatigue-Resistance of Low-Alloy Nickel-Chromium-Molybdenum Steel Forgings

G. E. DIETER, D. L. MACLEARY and J. T. RANSOM: 'Factors Affecting Ductility and Fatigue in Forgings', pp. 101–40; disc., pp. 140–2.

Tensile ductility and fatigue strength exhibit minimum values when determined in the transverse direction of steel forgings, and the steel-making and fabricating practices used to produce the forgings are known to be influential in this respect. This paper presents data relating to the transverse ductility and fatigue strength of steel forgings and to the influence of steel quality on the anisotropy of these properties.

The data on ductility (of low-alloy steels and chromium stainless steels) were derived almost entirely from the literature, and much of the discussion refers to work on the ductility of gun forgings carried out during World War II at the Carnegie Institute of Technology. Anisotropy of ductility is reviewed first in terms of its causes in wrought products in general, and then in relation to the effects of inclusions, second phases and segregation in forged steels.

Very little information on transverse fatigue properties is available in the literature. In the present paper the subject is considered by the authors on the basis of data obtained during a comprehensive investigation of the fatigue behaviour of steel forgings conducted over the past 10 years by E. I. du Pont de Nemours and Company, Inc. The three types of

specimen studied (torsion specimens, and full-size and half-size bend specimens) were taken from bars forged from seven heats of nickel-chromium-molybdenum steel of A.I.S.I. 4340 aircraft-quality grade. Vacuum-melted heats were included in the tests. Metallographic studies were carried out to determine the mechanism of failure associated with the test conditions. The influence of the following variables on the anisotropy of the fatigue limit was investigated: stress, specimen orientation, strength level of the specimen, deoxidation practice, and forging ratio.

In the concluding section of the paper the authors comment upon data derived from a statistical determination of the transverse fatigue limits of two A.I.S.I. 4320 nickel-chromium-molybdenum steels (modified, respectively, with boron and rare-earth additions) and of two low-carbon martensitic nickel-chromium-molybdenum-vanadium steels.

The authors' conclusions are quoted below:

'(1) Both the tensile ductility and the fatigue limit of forgings have minimum values in the direction transverse to the principal direction of working. The transverse values may be considerably lower than the longitudinal values and are much more sensitive to all of the steelmaking variables.

'(2) The transverse ductility is influenced primarily by the type, size, and distribution of the nonmetallic inclusions. Except for the extremes of very poor practice or very good practice, the number of inclusions is of secondary importance. Deoxidation practice affects the type of inclusions. Forging reduction affects the shape of inclusions. Factors not yet investigated in the time-temperature sequence of steelmaking practice must have primary effects on the nature of the inclusions and, therefore, on the quality of the forged product.

'(3) Transverse ductility is influenced by macro- and microsegregation of both metallic and nometallic constituents. Ferrite banding from segregation or, in the case of certain stainless steels, from the presence of an equilibrium second phase, can markedly reduce transverse ductility.

'(4) The transverse fatigue limit is even more sensitive to steel-making practice than is the transverse ductility, and good transverse ductility does not necessarily mean good transverse fatigue strength. While the nonmetallic inclusions and the steelmaking variables are important factors in determining the transverse fatigue limit, their relative importance is not clear; apparently there are some unknown factors which can exert strong influences.

'(5) Nonmetallic inclusions adversely affect both longitudinal and transverse fatigue limits. Size is the controlling characteristic of nonmetallic inclusions for the longitudinal fatigue limit. The controlling characteristic for the transverse fatigue limit is not clear. Differences in deoxidation practice, ingot size, forging reduction, and location of specimens in the ingot result in large differences in fatigue limits, but these cannot yet be correlated directly with any single inclusion characteristic. The virtual elimination of nonmetallic inclusions invariably results in high transverse and longitudinal fatigue limits.

'(6) The anisotropy in fatigue limit increases with increase in strength level to which the forging is heat-treated. Ultra-high tensile strength may not necessarily result in higher transverse fatigue limit.

'(7) Plain silicon deoxidation results in a superior transverse fatigue limit compared to aluminium-silicon deoxidation.

'(8) For aluminium-deoxidized steels, larger ingot sizes unexpectedly resulted in higher fatigue limits. While direct correlation with inclusion type, size or number was not possible, larger ingots showed lower total oxygen content.

'(9) The transverse fatigue limit decreases as the location of the specimens moves toward the centre of the bar. No significant variation of transverse fatigue limit could be observed for different positions in the original ingot.

'(10) Increased forging reduction generally reduces the transverse fatigue limit, but the decrease is not so pronounced as is the decrease in tensile RAT (reduction of area transverse) with forging reduction.

'(11) Rare-earth additions had a small beneficial influence on the transverse fatigue limit. Further research might demonstrate conditions which would result in greater benefits.'

Relationship between Inclusions and Rolling Fatigue in Ball Bearings

H. HUBBELL and P. K. PEARSON: 'Nonmetallic Inclusions and Fatigue under Very High Stress Conditions', pp. 143–51; disc., pp. 151–3.

The investigation described was carried out on ball-bearing outer raceways in A.I.S.I. 52100 high-carbon chromium steel.

Quality Control in the Production of Nickel-Chromium-Molybdenum Steel

B. M. SHIELDS: 'Meeting Cleanliness Requirements of Super-Duty Steels', pp. 167–78; disc., 178–81.

On the assumption that electric-furnace production of steel required to meet aeronautical specifications confronts the steelmaker with one of the most difficult problems of quality control, the author has based his paper on data relating to the production of A.I.S.I. 4340 nickel-chromium-molybdenum low-alloy steel for aircraft forgings and of Type 410 chromium stainless steel for extrusion into jet-engine rings.

Criteria of 'steel cleanliness' are first defined, and then, in the main sections of the paper, the author comments upon the melting variables which influence the 'cleanliness' of the two representative steels discussed, and outlines the requirements which the melting practice must satisfy to ensure production of the so-called 'super-duty' steels. In his practical recommendations the author lists no fewer than twelve factors which must be closely controlled if cleanliness' requirements for the low-alloy steel are to be consistently met.

Control of Segregation and Ingot Structure in Nickel-Chromium-Molybdenum High-Strength Steel

J. G. MRAVEC: 'Control of Segregation and Ingot Structures in Low-Alloy Steels', pp. 183–206; disc., pp. 206–9.

The investigation reported was undertaken to determine the influence of ingot size on the microstructure and distribution of alloying elements in ingots of A.I.S.I. 4340 nickel-chromium-molybdenum low-alloy steel.

The seven ingots studied were cast from the middle portions of 90-ton electric-furnace heats deoxidized with aluminium to meet specifications calling for fine grain-size. In section size they ranged from 16 in. × 16 in. to 24 in. × 24 in., and they varied in weight from 3200 to 9840 lb.

The ingots were split longitudinally and etched to reveal the macrostructure. The longitudinal, etched sections of all the ingots, irrespective of shape or size, exhibited the typical herringbone structure in the central core area. The ratio of herringbone length to ingot-body length decreased with decrease in the ratio of ingot-body length to mean cross-sectional diameter: i.e., the use of squat moulds helps to decrease the length of the herringbone structure encountered in ingots.

In ingot-chemistry studies, the longitudinal section of one cold-poured ingot, and of others poured at normal temperature, was drilled at twenty-one different positions. Ingots poured at normal temperature were found to be chemically homogeneous throughout, but the cold-poured ingot exhibited considerable chemical segregation at various positions (carbon segregating to the greatest degree). Negative segregation was confined mainly to the bottom portion of the ingot, while positive segregation tended to be more prevalent in the upper portion. Correct temperature control of the metal is considered to be unquestionably the most effective means of ensuring good homogeneity in ingot chemistry.

The procedures employed during the study are described in detail and the data obtained are reported *in extenso*.

Vacuum De-gassing of Nickel-containing Forging Steels

M. A. OREHOSKI and J. N. HORNAK: 'Effect of Vacuum Stream Degassing on Properties of Forging Steels', pp. 235–58; disc., pp. 258–66.

With the aim of finding some means of lowering the hydrogen content of steel intended for large forgings, and thus preventing the development of thermal flakes and ensuring achievement of the desired tensile ductility, the United States Steel Corporation initiated exploratory experiments to determine the effects of prolonging the heat-treatment cycle or modifying the steelmaking practice. Since neither procedure reduced the hydrogen content to a level (<1·5 p.p.m.) associated with optimum tensile ductility at the strength levels required in forgings for rotor applications, research was subsequently directed towards the development of vacuum procedures capable of de-gassing forging steels. The vacuum stream de-gassing (vacuum-casting) procedure finally evolved, and the results obtained by its use, form the subjects of the present paper.

The vacuum-casting equipment is described and illustrated, and details are given of the procedures employed and the operational variables involved. Data are presented to exemplify the casting procedures used for, and the effects of the operational variables on, ingots (from 7 to 160 tons in weight) of steel of the following types: nickel-molybdenum-vanadium and chromium-molybdenum-vanadium rotor steels, nickel-chromium-molybdenum-vanadium, manganese-nickel-molybdenum and nickel-chromium-molybdenum steels, and low- and high-chromium steels of, respectively, A.I.S.I. 52100 and 422 grade Notes and data are included on operating pressures, the gases and fume evolved during vacuum casting, and the importance of temperature control.

The final section of the paper outlines the beneficial effects of vacuum casting, as reflected in the properties of vacuum-cast steels. Emphasis is placed on the condition of the ingot surface, sensitivity to flaking, soundness, cleanliness and alloy segregation, tensile properties, and reductions achieved in the hydrogen, oxygen and nitrogen contents.

Vacuum Melting of Steels

A. M. AKSOY: 'Quality Aspects and Properties of Vacuum-Melted Super-Duty Steels', pp. 267–83.

In this paper the author discusses the vacuum-melting processes at present in use, describes the equipment and procedures associated with vacuum-induction melting and vacuum-arc remelting (the two techniques with which the review is principally concerned), and compares the quality of vacuum-melted steels and alloys with that of materials melted by conventional processes.

Vacuum melting is stated to be employed mainly to (1) lower gas content, (2) control composition, (3) improve cleanliness, (4) obtain ingot structures free from centre porosity and segregation, (5) produce metals and alloys which cannot be melted (or subsequently economically hot-worked) by conventional techniques. These objectives are considered, and the degree to which they can be achieved is exemplified by data on various low- and high-alloy steels.

Vacuum Induction Melting of Low-Alloy Steels

B. F. RICHARDSON: 'The Vacuum Induction Melting of Low-Alloy Steels', pp. 285–93; disc., 293–5.

The vacuum-induction-melting practice adopted by Kelsey-Hayes Company for production of low-alloy steels is exemplified in terms of the procedure used to melt bearing steel of A.I.S.I. 52100 type.

Steel for Aeronautical Applications: Quality Requirements

W. J. HARRIS: 'Super-Duty Steel Quality, Present and Future', pp. 297–301.

In this concluding paper of the Conference the author discusses some of the factors involved in satisfying the demands of the aircraft industry for material of the highest quality.

Influence of Nickel and Manganese on the Impact-Resistance of Medium-Carbon Cast Steels

I. B. ELMAN and R. D. SCHELLENG: 'Impact-Resistance of Nickel-Manganese Cast Steels.'
Modern Castings, 1960, vol. 37, Feb., pp. 67–70.

Steels meeting the requirements of Grade 'C' specification of the American Association of Railroads are typical of the many used, in the form of castings, at strength levels in the region of 90,000 p.s.i. (40 t.s.i.; 63·5 kg./mm.²) and under conditions of dynamic loading. Impact-resistance is of primary importance (during winter, for example, castings are frequently subjected to impact at low temperatures). In view of references in the literature to improvements in toughness achieved by addition of nickel and manganese, the investigation now described was initiated to obtain information on the conjoint effects of the two elements on the impact characteristics of normalized-and-tempered medium-carbon steels.

The manganese and nickel contents of the 21 induction-melted heats studied were varied in the range 0·5–1·5 and 0–1·5 per cent., respectively. The carbon content was maintained at 0·3 per cent. To determine the influence of deoxidation practice on impact-resistance, 14 of the heats were deoxidized with silicon and manganese, the remainder with silicon, manganese and aluminium. Impact-resistance was determined also as a function of the section size of the castings.

Charpy V-notch and, in some cases, tensile specimens were machined from keel blocks. Impact tests were conducted at 0°, −25°, −50° and −75°F. (−18°, −30°, −45° and 60°C.).

The data presented (which are supplemented by photomicrographs illustrating the structure of representative heats) demonstrate that, in the case of a silicon/manganese-deoxidized steel containing 0·5 per cent. manganese, the 15 ft. lb. transition temperature decreased from above 36°F. (2°C.) to −50°F. (−45°C.) as the nickel content was increased from 0 to 1·5 per cent. In the absence of nickel, manganese first lowered and then increased the transition temperature. Nickel additions to steels containing 1·25–1·5 per cent. manganese caused a sharp reduction in the transition temperature, and the transition temperatures of those containing more than 0·5 per cent. nickel were below −30°F. (−35°C.).

Manganese was found to be more effective than nickel in increasing tensile and yield strength. A steel containing 1·5 per cent. manganese and 1·5 per cent. nickel exhibited the following tensile properties:

Tensile strength	91,000 p.s.i. (40·5 t.s.i.; 64 kg./mm.²)
Yield strength	62,000 p.s.i. (27·5 t.s.i.; 43·5 kg./mm.²)
Elongation	27 per cent.
Reduction in area	56 per cent.

Steels having a somewhat lower nickel and higher manganese content exhibited similar properties: impact-transition temperatures were below −50°F. (−45°C.). (The minimum transition temperature obtained with the steels containing only manganese was +3°F. (−16°C.).)

Steels deoxidized with silicon, manganese and aluminium exhibited lower impact-transition temperatures than those deoxidized with silicon and manganese.

The impact-resistance of large castings was lower than that of smaller castings in the same material. It is noted, however, that variation in section size had a less pronounced effect on impact properties in the case of steels of higher nickel content.

Use of Nickel-Chromium-Molybdenum Steel in the Construction of the Bathyscaphe

E. VON DER LADEN: 'Designed for 1200 Atmospheres: the Construction of Jacques Piccard's Bathyscaphe.'
V.D.I. Nachrichten, 1960, vol. 14, Feb. 13, pp. 1 and 4.

On the 23rd January, 1960, Jacques Piccard and Lt. Walsh dived to a depth 11,521 metres below the surface of the Pacific Ocean. At this depth the 'bathyscaphe' in which the feat was accomplished was subjected to a pressure of about 1200 atmospheres. The factors involved in the design, construction, testing and operation of the metallic sphere which was to withstand these pressures form the subjects of the present article.

The sphere, which was fabricated by the firm of Friedrich Krupp, was assembled from three forged parts machined to extremely close tolerances. An electric-arc-melted and vacuum-cast steel of the following composition was selected as material of construction: carbon 0·35, silicon 0·25, manganese 0·4, phosphorus 0·035, sulphur 0·035, nickel 1·5, chromium 1·5, molybdenum 0·25, per cent. A scale model of the sphere, tested to destruction under an external load, imploded at a pressure of 2200 atmospheres (i.e., at a pressure almost twice that to which resistance was required).

Check-Analysis Limits for Wrought Low-Alloy Steels

SOC. AUTOMOTIVE ENGINEERS: 'Chemical Check Analysis Limits: Wrought Low-Alloy and Carbon Steels.'

Aeronautical Material Specification 2259, issued Jan. 15, 1960.

The purpose of the specification is to 'publish standard chemical check-analysis limits, as established by A.I.S.I. or A.M.S. usage, and to correlate their application and use with material specifications'. The percentage limits specified for the various constituent elements listed are correlated with the amount by which an individual determination may vary above or below the limits. The check analysis is made after the material has been worked into semi-finished or finished forms or fabricated into parts, and is used either for the purpose of verifying the composition of a heat or to determine variations in composition within a heat. It may be used as a

basis for acceptance or rejection of a heat of material or batch of parts.

In the case of carbon-steel bars, forging stock, wire (other than flat) and seamless tubing, check limits are specified for carbon, manganese, silicon, phosphorus, sulphur, copper and lead. In the case of carbon-steel sheet, strip, plate, flat wire and welded tubing, limits for lead are not included. Variations for low-alloy steels are classified according to cross-section size and relate to the following elements: carbon, manganese, silicon, phosphorus, sulphur, chromium, nickel, molybdenum, tungsten, aluminium, vanadium, copper and zirconium.

HEAT- AND CORROSION-RESISTING MATERIALS

Quality Requirements of Super-Duty Steels: Symposium

AMER. INST. MINING, METALLURGICAL AND PETROLEUM ENGINEERS: 'Quality Requirements of Super-Duty Steels.'

Metallurgical Soc. Conferences, 1959, vol. 3; 309 pp. Published by Interscience Publishers, Inc., New York; Interscience Publishers, Ltd., London.
Price, $8.50; 64/-.

This volume contains the proceedings of the Technical Conference held, under the aegis of the American Institute of Mining, Metallurgical and Petroleum Engineers, at Pittsburgh, May 1958.

Many of the papers contained in the volume relate mainly to structural steels; others are, however, concerned exclusively with steels of high-alloy content. In here indicating the scope of the Conference, an attempt has been made to classify the papers on the basis of their predominant subject matter. *Accordingly, those which relate mainly to stainless and high-alloy steels are referred to below, while abstracts of papers covering low-alloy structural steels (or of those which are of general interest) will be found in the relevant section of this issue, pp.* 109-111.

Reference is made to all the papers presented at the Conference, but considerations of space preclude any but a brief outline of their scope.

Requirements of 'Reactor-Grade' Materials

R. C. DALZELL: 'Commercial Production of Reactor-Grade Materials', pp. 33-7; disc., pp. 37-9.

An explanation of the reasons for the stringent specifications covering materials intended for service in nuclear reactors (emphasis is placed on the toxicity of the fission products and the impracticability of carrying out maintenance on components exposed to radioactivity) leads the author to examine the problems associated with the achievement of the requisite close control over composition. Reference is made to such 'reactor-grade' materials as low-cobalt stainless steel, an aluminium-base alloy, and the nickel-base alloy 'Inconel CX-900'. In the latter material, a modification of the normal grade of 'Inconel', the aluminium and titanium content is maintained below 0·5 per cent., and the carbon content between 0·02 and 0·7 per cent., with the aim of improving brazing characteristics.

Stainless and Hot-Work Die Steels for High-Strength Applications

A. J. LENA and F. A. MALAGARI: 'Stainless Steels and Hot-Work Die Steels for High-Strength Applications'. pp. 43-67; disc., pp. 68-79.

The paper comprises a review of the types of stainless and tool steels now in, or under consideration for, use as materials of construction for airframes. It is concerned almost entirely with the effects of composition and structure, and no attempt is made to provide detailed information on the engineering properties of the steels.

Four types of steel are considered: hot-work die steels, martensitic-hardenable stainless steels, precipitation-hardenable stainless steels, and cold-rolled austenitic stainless steels. Although data are included on a range of representative materials, the points raised are illustrated mainly in relation to the chromium-molybdenum-vanadium die steel 'Potomac A', A.I.S.I. Type 419 chromium-tungsten-nickel-molybdenum-vanadium martensitic stainless steel, the chromium-nickel-molybdenum precipitation-hardenable stainless steels 'AM-350' and 'AM-355', and cold-rolled 17-7 Type 301 austenitic stainless steel.

Effects of Radiation on Stainless Steels

D. E. THOMAS: 'Radiation Damage in Ferrous Materials', pp. 81-95; disc., pp. 95-9.

The behaviour of steels under irradiation is first discussed in relation to the mechanisms proposed in explanation of radiation damage. The effects of irradiation are then particularized in terms of data illustrating the changes which result in the mechanical properties of pure iron, carbon steel, various grades of chromium-nickel austenitic steel, and Type 410 straight-chromium stainless steel.

Analysis Control of '17-7 P.H.' Stainless Steel

L. F. WEITZENKORN: 'Analysis Control of '17-7 P.H.' Stainless Steel', pp. 157-62; disc., pp. 162-5.

The attractive properties of the precipitation-hardenable stainless steels are a function of their microstructure, which, in turn, is governed by chemical composition and heat-treatment. Control of composition in arc melting such steels is therefore of utmost importance. The present paper gives full details of the melting practice adopted by Armco Steel Corporation to exert the necessary control over composition during the production of commercial heats of '17-7 P.H.' stainless steel.

Data are presented to illustrate the importance of mixing the bath before taking samples, and methods of stirring large arc furnaces and sampling the bath

are noted. The efficacy of the procedures used is indicated by data summarizing the results of ladle analyses of one hundred heats of '17-7 P.H.'

Hot Working of Iron-, Cobalt-, and Nickel-base Materials

H. FREEMAN and T. N. KELLEY: 'Hot Working of Super-Duty Alloys', pp. 211-27; disc., pp 227-31.

In the introductory section of their paper the authors allude to the considerable improvements achieved during recent years in the hot-working characteristics of many conventional steels and alloys, and emphasize, in this connexion, the beneficial effects associated with close control of production and processing variables. Control considerations play an even more important rôle in the production of 'super-duty' alloys and steels, and consequently the variables involved in the hot working of ingots, blooms and billets of iron-, nickel- and cobalt-base materials representative of such grades are selected for discussion in the present paper.

The paper is divided into sections covering the following factors: *Tests used to determine hot workability* (upset, hot-tensile, impact, hot-twist and hot-bend tests); *Variables influencing hot-working properties of ingots* (composition, melting method, ingot quality, heating practice and atmosphere control, hot-working temperatures, working methods and reductions); *Billet practice* (temperature range, billet preparation, reductions and rolling-pass designs); *Typical practices used to process S-816' (cobalt-base-alloy) ingots to bar*; *Hot working of molybdenum.*

The following materials are selected as representative of the classes discussed and, throughout the review, are cited by the authors to particularize or illustrate the information presented: '19-9DL'; '19-9DX'; 16-25-6'; 'S-816'; 'L-605'; 'Unitemp HX'; 'N-155'; 'A-286'; 'Waspaloy'; 'M-252'; 'Unitemp 500'; 'Unitemp 901'.

Intergranular Cavitation, Structure and Creep of 'Nimonic 80A'

C. W. WEAVER: 'Intergranular Cavitation, Structure, and Creep of a 'Nimonic 80A'-type Alloy.

Jnl. Inst. Metals, 1960, vol. 88, Mar., pp. 296-300.

Previous investigations have demonstrated that the creep behaviour of alloys of 'Nimonic 80A' type is influenced by heat-treatments which control the distribution of a carbide phase. When the solution temperature is raised from 1080° to 1200°C. the precipitation of a chromium-carbide phase can be controlled by application of certain ageing treatments. Ageing after quenching from solution-treatment disperses the carbide finely within the grains (giving high hardness), whilst ageing directly at 950°C., without quenching from 1250°C., induces continous dense precipitation of an intimate mixture of chromium carbide and the γ' phase at the grain boundaries (associated with long times to rupture and higher elongation). BETTERIDGE and FRANKLIN have attributed the beneficial effects of intergranular carbide to local chromium impoverishment in the matrix adjacent to the boundaries, which permits greater deformation in these regions (see abstract in *Nickel Bulletin*, 1957, vol. 30, No. 7-8, pp. 129-30). Recent models of the mechanism of intergranular creep cracking suggest, however, that it is the rate of nucelation and growth of intergranular cracks which is important (see, for example, GIFKINS, *Acta Metallurgica*, 1956, vol. 4, p. 98). The metallographic study now reported was carried out in an attempt to obtain information which would throw light on this problem.

Specimens of laboratory-produced 'Nimonic 80A', approximating to the following composition, were fractured in creep at 750°C. in several conditions of heat-treatment, and then subjected to metallographic examination: nickel 75, chromium 20, titanium 2·5, aluminium 1·5, carbon 0·015-0·08, per cent.

The findings of this study are summarized as follows:

'Correlations have been found between composition (particularly carbon content), microstructure (arising from heat-treatment), the type and number of cracks produced during creep, time to rupture, and elongation, which suggest that the influence of microstructure on creep behaviour operates through its influence on the mechanism of crack nucleation and growth.

'Two types of cavity were found, depending on the carbon content and heat-treatment. Triple-point cracks occurred in low-carbon heats after the specification heat-treatment, and widespread intergranular cavitation in heats containing 0·03 per cent. carbon or more, after direct ageing at 950°C. from solution-treatment at 1200°C.

'Specimens with high elongation and long times to rupture (i.e., specimens directly aged) contained many cavities, and specimens exhibiting brittle fracture (i.e., water-quenched specimens) contained only a few, such that a linear relationship existed between the cavity volume per unit boundary area, elongation at fracture, and time to rupture. Hence, the rate of elongation on a fracture-time basis was constant.

'The influence of grain-boundary structure on cavitation may be explained in terms of recent hypotheses of crack nucleation, particularly that of Gifkins (*loc. cit.*), in which cavities arise from a combination of grain-boundary sliding and slip across the boundary. The presence of large particles of carbide in the grain boundaries serves both to nucleate cavities at, and restrict them to, the inter-carbide spaces, from which, by virtue of the good fit across the carbide/grain interface, they have difficulty in spreading. The amount of grain-boundary sliding (and hence the total elongation) occurring before fracture is thereby increased, and the time required for the cavities to extend round the sides of the carbide precipitates increases also, thus increasing time to rupture.'

Recrystallization of a Molybdenum Alloy: Influence of Nickel Plating

See abstract on p. 108.

Sigma Phase in the Chromium-Iron and Chromium-Nickel Systems

H.-J. SCHULLER and P. SCHWAAB: 'An Electronoptical Study of the Sigma Phase in the Chromium-Iron and Chromium-Nickel Systems.

Zeitsch. f. Metallkunde, 1960, vol. 51, Feb., pp. 81–4.

Vacuum-deposited films of 45–55 chromium-iron and 70–30 chromium-nickel alloys were heated *in vacuo* for various times and at various temperatures and then examined, by electron-diffraction techniques, to determine the presence of sigma phase.

In the case of the chromium-iron films, sigma-phase formation was established with certainty at temperatures down to 350°C., and with high probability at 300°C., findings which, it is considered, do not appear to justify (at least for temperatures above 300°C.) the postulation of a eutectoid breakdown of sigma phase. The upper temperature limits of the phase boundaries could not, however, be determined, since, due to the high reaction rates inherent in the thin films studied, transformation could not be prevented even by quenching.

The presence of sigma was determined also in the chromium-nickel films after exposure to temperatures in the range 400°–950°C. As with the chromium-iron films, however, the upper limits for the existence of the phase could not be ascertained.

Suitability of 'Inconel' for Nuclear-Power Applications

H. R. COPSON and W. E. BERRY: 'Qualification of 'Inconel' for Nuclear-Power-Plant Applications.'

Corrosion, 1960, vol. 16, Feb., pp. 79t–84t

Materials of construction used in the steam-generation system of pressurized-water nuclear-power plants must satisfy stringent requirements. The materials are exposed on one side to primary reactor water (heat-exchange medium flowing past the radioactive fuel elements), and on the other side to secondary boiler water. On the primary side, corrosion products may be transported to the fuel elements, activated, and then transported back. It is imperative, therefore, that there be a minimum of loose corrosion products, that the induced radioactivity of these products below, and there that be no mixing of the two kinds of water. To satisfy these requirements a material of construction should exhibit excellent fabrication characteristics, good corrosion behaviour and suitable physical and mechanical properties. The austenitic steels, which have been used extensively in such applications, are susceptible to stress-corrosion cracking under certain conditions, and there was some risk that these conditions might be encountered in heat-exchanger systems. The nickel-chromium-iron alloy 'Inconel' is reported to resist stress-corrosion cracking in chloride and alkaline environments, and the corrosion tests reported were therefore carried out as part of a programme to evaluate the suitability of the alloy for use in nuclear-power plants. (Details of the findings of the radiochemical and welding phases have already been given: see SOLOMON and VOGEL, *U.S. Atomic Energy Commission Report W.A.P.D.-T-900* and paper by FRAGETTA and PEASE abstracted in *Nickel Bulletin*, 1959, vol. 32, No. 6, p. 204.)

The tests were conducted using simulated primary water and simulated secondary boiler water. The primary-water tests were carried out both in a high-velocity loop and in autoclaves. Specimens from

Corrosion of 'Inconel' and Stainless Steel in Primary and Secondary Waters

(*See abstract on this page.*)

Test	Temperature °F.	Temperature °C.	Exposure Time Hour	Average Corrosion Rate After First Period mg./dm.²/month					
				'Inconel'			Type 347		
Tests with Primary Water									
1	550	290	500, 1000, 1500, 2000	8·8			7·4		
2	650	345	500, 1000, 1500, 2000	7·6			10·1		
3	550	290	200, 500, 1000, 2000	1·5			5·4		
4	550	290	500	9·2*			12·7*		
5	550	290	200, 500, 1000, 2000	1·0			—		
6	600	315	200, 500, 1000, 2000	1·1			—		
7	680	360	200, 400, 500, 700, 1000, 1200, 2000, 2200	2·7			4·4		
Tests with Secondary Water				Vapour	Interface	Liquid	Vapour	Interface	Liquid
8	500	260	2000	5·8†	11·1†	10·0†	28·3†	22·3†	18·7†
9	500	260	200, 500, 1000, 2000	3·2	3·9	3·9	5·0	8·9	7·0

* Weight loss in 500 hours (mg./dm.²) † Weight loss in 2000 hours (mg./dm.)²

the three heats of 'Inconel' selected for study (a normal mill-production heat, a heat of unusually high carbon content, and a heat of unusually low chromium content) were subjected, prior to testing, to different heat-treatments to determine their effects on corrosion-resistance. Type 347 18-8-Nb stainless steel was included in the test programme as a reference material.

The duration and the temperature of the tests, and the average corrosion rates determined, are given in the table on page 115.

The primary water contained 2-3 p.p.m. of ammonia and (except in tests (4), (5) and (6), in which the hydrogen was deliberately omitted) 25-65 cc. of hydrogen. The oxygen content was generally less than 0·02 p.p.m. (except in test (4) where the water was saturated with oxygen at start-up). The pH was between 8·8 and 9·7. The secondary water contained about 50 p.p.m. of chloride and 120-150 p.p.m. of phosphate. The pH was adjusted to the range 10·6-10·8, and the solution was saturated with air at start-up.

Tests (1) and (2) comprised loop tests, in primary water, on specimens which included, for the 1,000-hour periods, crevice specimens. The autoclave tests in primary water (tests (3)-(7)) involved exposure of: weight-loss, stress-and-crevice and cross-weld specimens and of galvanic couples (tests (3) and (4); weight-loss specimens of the standard alloy (tests (5) and (6)); standard weight-loss, stress-and-crevice and cross-weld specimens (test (7)). In the autoclave tests in secondary boiler water (tests (8) and (9)) identical sets of specimens were exposed in the liquid and vapour phases and at the liquid/vapour interface: test (8) involved the same types of specimen as test (3); weight-loss specimens were exposed in test (9).

The authors regard the data presented as ample evidence, from the corrosion point of view, of the suitability of 'Inconel' for use as a material of construction in primary and secondary waters of pressurized-water reactors. The alloy formed tightly adherent tarnish films and contributed a relatively minor amount of corrosion product to the high-velocity stream of primary water. It corroded at rates comparable to those of Type 347 stainless steel.

Variations in composition and heat-treatment had little effect on the corrosion behaviour of the alloy in either primary or secondary waters, and welding, or the presence of stress or crevices, did not cause selective or intergranular attack. Galvanic coupling of 'Inconel' with steel or stainless steel did not accelerate the corrosion of either member of the couples.

Oxidation of Heat-Resisting Steels in the Presence of Alkali-Sulphate Combustion Products and Sulphur (VI) Oxide

A. RAHMEL: 'Oxidation of Heat-Resisting Steels: Influence of Alkali-Sulphate Deposits in the Presence of Traces of Sulphur (VI) Oxide in the Furnace Atmosphere.'

Archiv f. d. Eisenhüttenwesen, 1960, vol. 31, Jan., pp. 59-65.

The work described originated in the unexpected occurrence of corrosive attack in the final superheater of a high-pressure-steam boiler. The results, which demonstrate that alkali-sulphate deposits on heat-resisting steels (particularly those of chromium-nickel type) can, if small amounts of sulphur (VI) oxide are present in the furnace atmosphere, result in severe oxidation at temperatures higher than 600°C.,

Composition of Heat-Resisting Steels

(See abstract above.)

Steel	C %	Si %	Mn %	Cr %	Ni %	Mo %	W %	V %	Co %	Ta+Nb %	N %
1	0·09	0·31	1·23	16·66	12·35	—	—	—	—	0·78	—
2	0·08	0·50	1·44	16·58	12·73	1·30	—	0·68	—	0·77	0·086
3	0·06	0·48	1·37	16·55	16·60	1·86	—	—	—	0·73	—
4	0·06	0·80	1·32	15·54	16·80	1·46	1·32	—	—	0·70	0·079
5	0·08	0·47	1·44	16·30	26·88	2·60	2·04	1·80	19·90	0·72	0·096
6	0·17	1·77	0·72	19·50	10·40	—	—	—	—	—	—
7	0·13	2·14	0·96	23·80	19·75	—	—	—	—	—	—
8	0·22	0·32	0·54	11·67	—	1·01	0·25	0·39	—	—	—
9	0·08	2·43	0·41	6·20	—	—	—	—	—	—	—
10	0·07	1·82	0·41	13·10	—	—	—		—	—	—
11	0·08	1·96	0·31	17·10	—		—	—	—	—	—
12	0·21	1·08	0·57	30·95	—	—	—	—	—	—	—

are considered of practical relevance to plant (e.g., those fired by oil) operating under conditions conducive to such attack. The attack on the superheater steels was tentatively attributed to the formation of a liquid phase on the surface of the steel and to the subsequent destruction of the protective oxide film. The investigation was carried out to determine the validity of this attribution.

The composition of the steels investigated are listed in the table on page 116. Steel (1) was the principal subject of study: the other steels were included in the test programme to establish the influence of composition. The specimens were immersed in high-purity potassium sulphate (or, in a few experiments, in a mixture containing 95 per cent. potassium sulphate and 5 per cent. Fe_2O_3) contained in a boat which was exposed to a stream of reaction gas (air, water vapour and sulphur (IV) oxide). The sulphur (IV) oxide was oxidated, in the presence of a catalyst, to sulphur (VI) oxide, the desired content of which was obtained by suitably modifying the concentration of the sulphur (IV) oxide or the temperature of the catalyst. The oxidation rate was established on the basis of the specimens' loss-in-weight. The influence of the following factors was studied: time and temperature of testing, the dew point of the reaction gas, the composition of the steel.

The data presented demonstrate that the rate of oxidation of the heat-resisting steels studied increased greatly at temperatures higher than about 625°C. Among the corrosion products involved in the reaction is a potassium-iron(III)-sulphate of the formula $K_3Fe(SO_4)_3$. This compound reacts with excess potassium sulphate to form a eutectic with a melting point (627°C.) which coincides with the temperature at which the oxidation rate increases.

The oxidation rate falls again at temperatures in the region of 800°C., a finding which is attributed to the instability of the potassium-iron-sulphate at these temperatures and the consequent absence of any liquid phase.

In the temperature range 625°–800°C. the oxidation followed a linear time law. An increase in the sulphur (VI) oxide content of the furnace gases increased the oxidation rate. The rate of oxidation fell with increase in chromium content, particularly in the case of chromium ferritic steels, and an increase in the silicon content had a similar beneficial effect. The presence of the alloying elements molybdenum and vanadium (which improve the heat-resistance of the steels) appeared, on the other hand, to be deleterious.

Oxidation of Nickel-containing Materials in Carbon Dioxide at High Temperatures and Pressures

J. C. BOKROS and W. P. WALLACE: 'High-Temperature, High-Pressure Oxidation of Alloys Caused by Carbon Dioxide.'

Corrosion, 1960, vol. 16, Feb., pp. 73t–8t.

Gas-cooled reactors are currently being designed with outlet temperatures in the range 1200°–1500°F. (650°–815°C.) and maximum fuel-cladding temperatures approaching 1800°F. (980°C.). Many gases have been considered for use as coolants in this type of reactor, and each involves problems of materials selection peculiar to the chemical nature of the coolant gas and its temperature and pressure. This paper reports some of the results obtained during a coolant-evaluation programme conducted in connexion with the Maritime Gas-Cooled Reactor project and involving screening tests in high-pressure, high-temperature carbon dioxide.

Four grades of material were evaluated:

(1) *Chromium-nickel austenitic steels* of 35-14, 25-20, 23-14, 18-8, 18-12Mo and 18-8Nb grade (i.e., A.I.S.I. Types 330, 310, 309, 304, 316 and 347).

(2) *Ferritic materials:* Straight-chromium stainless steels, chromium-molybdenum steels (chromium contents ranging from 1¼ to 9 per cent.), an iron-aluminium-chromium-niobium alloy ('DB-2'), an iron-chromium-aluminium alloy (Fe-Cr-Al), and a molybdenum steel.

(3) *Nickel-base Alloys:* 'A' nickel, 'Inconel', 'Inconel X', 'Nichrome V', 'Hastelloy B' and 'Nimonic 80'.

(4) *Miscellaneous Materials:* the cobalt-base alloy 'Haynes 25', niobium, a niobium-zirconium alloy and a niobium-molybdenum-titanium alloy.

The materials were tested in a static carbon-dioxide system at (1) a pressure of 2,000 p.s.i. and temperatures of 1300° and 1500°F. (705° and 815°C.) and (2) a pressure of 1,000 p.s.i. and temperatures of 1100° and 1740°F. (595° and 950°C.).

The data presented are interpreted as follows:

'(1) Weight-gain data, a measure of gross oxidation rates, revealed that all heat-resistant alloys tested at 1200° and 1500°F. oxidized slowly enough to be considered for use in the M.G.C.R.; i.e., all of the scales are protective.

'(2) Metallographic examination, however, revealed that certain materials were subject to localized attack: namely, pitting and intergranular attack. These materials therefore were eliminated from consideration. They included Types 304, 347, 310 and 330 stainless steel and 'Nichrome V'.

'(3) Type 446 was eliminated by scale-adherence-test results, the large amount of sigma formed, excessive grain growth, low strength and poor fabricability.

'(4) The remaining materials can be ranked according to high-temperature strength, structural stability and neutron cross section. Type 316 has better high-temperature strength than Type 309 and less propensity for sigma formation. It has a lower neutron-capture cross section than the nickel-base alloys such as 'Inconel' and 'Inconel X'. Among the ferritic materials, Types 405 and 430, 'DB-2', and Fe-Cr-Al exhibited good corrosion-resistance but have poor creep strength and are subject to grain growth at 1500°F. 'DB-2' and Fe-Cr-Al have not

been fully developed and present fabrication difficulties. Therefore, Type 316 and 'Inconel' should be considered tentatively for high-strength, fuel-cladding materials.'

Corrosion Products of Nickel and Nickel Alloys: Bibliography

'Bibliographies of Corrosion Products.'

Corrosion, 1960, vol. 16, Mar., pp. 131t-5t.

N.A.C.E. Technical Committee Report, Publication 60-4.

The five annotated *bibliographies* presented are concerned with literature on the corrosion products of the following metals and their alloys: cobalt, copper, chromium, molybdenum and nickel. They are intended to serve as an introduction to the subject, and therefore include only basic papers and others of particular interest. References to the items comprising the *bibliography* on nickel and its alloys are listed below.

S. YAMAGUCHI: 'The Investigation by Electron Diffraction the Corrosion of Metals.'

Bull. Chemical Soc. Japan, 1943, vol. 18, pp. 53-91.

A. P. C. HALLOWES and E. VOCE: 'Attack of Various Superheated Steam Atmospheres Upon Aluminium-Bronze Alloys.'

Metallurgia, 1946, vol. 34, July, pp. 119-22.
Based on *Brit. Non-Ferrous Metals Research Association Report R.R.A.* 527, *Part* II.

W. FEITNECHT: 'Corrosion of Metals in Acid Fumes.'

Schweizer Chemikerzeitung, 1946, vol. 29, Oct., pp. 332-3.

W. FEITKNECHT: 'Attack of Metals by Moist Vapours of Halogen Acids.'

Helvetica Chimica Acta, 1946, vol. 29, Dec. 2, pp. 1801-15.

U.S. PANAMA CANAL SPECIAL ENGINEERING DIV.: 'Long-Term Metals Corrosion Investigation.'

1*st Interim Report*, 1947, No. 74, Jan., 78 pp.; *Appendix I*, 167 pp.

H. A. PRAY, F. W. FINK and R. S. PEOPLES: 'Literature Review on Corrosion of Metals and Materials by Flue-Gas Condensate.'

Amer. Gas Association, Report No. 1, *Project DGR-4CH*, Feb. 1947; 29 pp.

H. N. POTTER: 'Condensate Return Line Corrosion Control.'

F. L. LAQUE: 'Some Notes on Corrosion in Condensate Return Lines.'

Modern Power and Engineering, 1947, vol. 41, May, pp. 47-8; Dec., pp. 47-8.

W. FEITKNECHT: 'The Breakdown of Oxide Films in Acid Vapors'

Proc. Pittsburgh International Conference on Surface Reactions, 1948, pp. 212-21.

W. A. WESLEY and H. R. COPSON: 'Effect of Non-Condensable Gases on Corrosion of Nickel in Steam Condensate.'

Jnl. Electrochemical Soc., 1949, vol. 95, May, pp. 226-41.

W. GUERTIER: 'Surface Problems of the Chemical Behaviour (Corrosion) of Metallic Materials.'

Metalloberfläche, 1949, vol. 3, No. 7, pp. 133-41.

W. FEITKNECHT: 'Fracture of Oxide Films on Metal Surfaces in Acid Vapour and the Mechanism of Atmospheric Corrosion.'

Chimia, 1952, vol. 6, pp. 3-13.

N. THON, L. YANG and S. YANG: 'Porosity of Electrodeposited Metals. XI. Analysis of Corrosion Products as a Method of Measuring the Change of Porosity in Corrosion.'

Plating, 1953, vol. 40, Sept., pp. 1011-15.

S. S. BRENNER: 'Oxidation of Iron-Molybdenum and Nickel-Molybdenum Alloys.'

Jnl. Electrochemical Soc., 1955, vol. 102, Jan., pp. 7-15.

S. S. BRENNER: 'Catastrophic Oxidation of Some Molybdenum-containing Alloys.'

Jnl. Electrochemical Soc., 1955, vol. 102, Jan., pp. 16-21.

H. W. VAN DER HOEVEN: 'Rate of Flow as Factor of Special Importance in Corrosion by Sulphuric Acid.'

Werkstoffe u. Korrosion, 1955, vol. 6, Feb., pp. 57-62.

R. W. HENKE: 'Progress Report of Task Group T-4F-1 on Water-Meter Corrosion.'

Corrosion, 1956, vol. 12, Jan., pp. 77-80.

Relationship between the Velocity of a Corrosive Environment and the Corrosion Behaviour of Metals

H. R. COPSON: 'Effects of Velocity on Corrosion.'

Corrosion, 1960, vol. 16, Feb., pp. 86t-92t.

In this review, which is based on a *bibliography* of 30 items, the author discusses the influence, on the corrosion behaviour of metals, of the velocity of the corrosive fluid.

Data (many of which relate to nickel-containing alloys and steels) are presented in support of the author's comments on the following factors: velocity; the relationship between velocity and the variables which influence the corrosion rate; the influence of velocity on the corrosion behaviour of iron and other materials; galvanic corrosion; erosion-corrosion of iron, copper alloys and other alloys; cavitation-erosion; velocity effects and electrochemical theory.

Corrosion of Steels in Marine Tropical Environments

B. W. FORGESON, C. R. SOUTHWELL and A. L. ALEXANDER: 'Corrosion of Metals in Tropical Environments. Part 3. Underwater Corrosion of Ten Structural Steels.'

Corrosion, 1960, vol. 16, Mar., pp. 105t-14t.

The test programme of which details are given in the present paper was undertaken as part of an extensive investigation, initiated in 1946 to provide data on the corrosion characteristics of fifty metals and alloys exposed in five different environments in the Panama Canal Zone. The ten steels studied (which included nickel-containing grades) were subjected to continuous immersion in fresh-water and sea-water, and to exposure in the Pacific Ocean at mean-tide elevation.

The information presented is similar to that contained in *U.S. Naval Research Laboratory Report N.R.L.* 5153: see abstract in *Nickel Bulletin*, 1959, vol. 32, No. 5, pp. 160-1.

Physical Metallurgy of Stress-Corrosion Fracture: Symposium

METALLURGICAL SOC., AMER. INST. MINING, METALLURGICAL AND PETROLEUM ENGINEERS: 'Physical Metallurgy of Stress-Corrosion Fracture.'

Metallurgical Soc. Conferences, 1959, vol. 4; 394 pp. Published by Interscience Publishers, Inc., New York; Interscience Publishers, Ltd., London. Price, 98/-; $13.

The papers and discussions contained in this volume comprise the edited proceedings of a Symposium which, arranged by the Committee on Corrosion-Resistant Metals of The Metallurgical Society of the American Institute of Mining, Metallurgical and Petroleum Engineers, with the aim of providing a 'forum for discussion among specialists from divergent fields and experiences in the solid-state sciences and in the technology of materials', was held at Pittsburgh in April 1959. The problem of stress corrosion was approached in two ways: the first half of the symposium was concerned

mainly with general principles relating the three basic factors of stress, fracture and chemical reactivity; the second half was directed towards clarification of the mechanisms of stress-corrosion cracking in terms of specific environments and materials.

The scope of the individual papers is indicated below.

Mechanism of Stress Corrosion

H. H. UHLIG: 'New Perspectives in the Stress-Corrosion Problem', pp. 1–16; disc., pp. 17–28.

General review of the factors which contribute to stress-corrosion cracking, involving discussion of the following points: the imperviousness of pure metals to such attack; the influence of impurities on the cracking of solid-solution alloys; similar types of cracking in which corrosion does not participate ('hydrogen cracking' and 'stress-sorption cracking'); theories advanced in explanation of stress-corrosion cracking.

In the author's consideration of the mechanism underlying stress-corrosion cracking, the electrochemical mechanism and the effects of plastic deformation receive particular attention. It is suggested that selective adsorption of ions which lower the surface energy of the crack might operate conjointly with electrochemical action along paths where defects predominate and where compositional gradients exist, resulting in a discontinuous rate of crack formation by alternate physical parting and electrochemical action.

Effect of Electric Strain on the Electrode Potential of Metals

L. YANG, G. T. HORNE and G. M. POUND: 'Effect of Electric Strain on the Electrode Potential of Metals', pp. 29–39; disc., pp. 39–46.

Measurements of electrode potential of uniaxially stressed pure metals (data derived from tests on iron, copper, gold, silver and mild-steel sheet, wire and discs are tabulated) show that tension renders the metal more noble, while compression renders it less noble: the magnitude of the potential shift is of the order of several tenths of a millivolt per 1000 lb./sq. in. The purpose of the present work is to 'review the relationships between stress and chemical potential in order to see in how far the unexpectedly large potential shifts, and their change in sign between tension and compression, may be simply explained in terms of thermodynamics'.

Surface Structure and Chemical Interaction

G. EHRLICH and D. TURNBULL: 'Surface Structure and Chemical Interaction', pp. 47–69; disc., pp. 69–70.

In this paper the authors review the equilibrium and actual structures of crystal surfaces, and discuss the way in which molecular interactions depend upon the nature of the sites present on the surface of real crystals in a dilute fluid. In considering molecular interactions they distinguish self-interactions (between molecules and a chemically identical lattice) from impurity interactions (in which chemically dissimilar molecules are involved).

Effect of Stress on the Corrosion Failure of γ-Phase Uranium Alloys

J. N. CHIRIGOS: 'The Rôle of Lattice Mismatch Between Oxide and Metal in the Corrosion Behaviour of Gamma Uranium Alloys', pp. 70–8.

This short paper is included in view of the fact that it presents experimental data and interpretations based on concepts of the Frank-Van der Merwe theory of oriented overgrowths, and is, to this extent, associated with the approach of Ehrlich and Turnbull (*see previous abstract*).

Crack Propagation During Stress Corrosion

C. EDELEANU: 'Crack Propagation During Stress Corrosion', pp. 79–91; disc., pp. 91–8.

The work described was conducted with the aim of assessing the validity of a theory, which, interpreting stress corrosion in terms of a partially mechanical failure, appears capable of explaining the main observed facts: i.e., that stress-corrosion cracking is apparently a brittle failure of alloys normally considered ductile; that the rate of cracking is low by physical standards but very high by normal standards of chemical attack; that certain alloys are particularly prone to this type of failure; and that the chemical conditions are specific for each case.

It is considered unlikely that these facts will be explained by theories based on the assumption that the main factor involved in stress corrosion is rapid penetration due to acceleration of corrosion by stress, and if rapid penetration by corrosion is not accepted, it is deemed necessary to postulate brittle fracture (in spite of the bulk ductility of the alloys in question). The present work (concerned with α brass in ammonia) supports the view that the cracks progress in short brittle fractures, and it is postulated that the function of corrosion is to assist in the initiation of brittle fracture and not to cause appreciable penetration. It is tentatively suggested that dezincification assists crack initiation, but other mechanisms may be associated with other alloy systems.

The fact that brittle cracks can run at all in ductile material is attributed, in the case of brass and copper-gold alloys, to the presence of short-range order and the resulting deceleration effect on dislocation movement, but it is again emphasized that other cases (particularly those of intercrystalline corrosion) may involve other mechanisms.

Stress Corrosion of α-Brass and Similar Alloys

A. J. FORTY: 'The Initiation and Propagation of Cracks in the Stress Corrosion of α-Brass and Similar Alloys', pp. 99–115; disc., pp. 115–7.

The mechanism proposed by Edeleanu (*see previous abstract*) is examined in terms of current metallurgical ideas and an assessment is made of its general significance to systems other than that of the α-brass/ammonia which is the main subject of the author's discussion.

Application of Electron Microscopy to Study of Stress Corrosion

G. A. BASSETT and C. EDELEANU: 'An Electron-Microscope Technique Applied to Stress Corrosion', pp. 117–20.

This note describes the authors' attempt to provide electron-microscopical evidence in support of Forty's explanation of stress corrosion of α-brass in terms of dislocation theory.

Rôle of Corrosion Products in Stress-Corrosion Cracking of Austenitic Steel

N. A. NIELSEN: 'The Rôle of Corrosion Products in Crack Propagation in Austenitic Stainless Steel. Electron-Microscopic Studies', pp. 121–43; disc., pp. 143–54.

The work reported in the paper originated in the author's postulation that insoluble corrosion products play a more important rôle in transgranular crack propagation than appears to have been reported in the literature. It is theorized that 'alloy corrosion products are cathodically deposited behind the apex of an advancing crack. By a simple wedging action, the precipitated material builds up stress within the crack to a threshold level at which the total strain energy, including residual and applied stresses, is suddenly released by propagation of the crack; the chloride-containing electrolyte is sucked into the enlarged crack and further corrosion of local anodes occurs, providing more soluble metal ions. These ions migrate toward the cathodic areas within the crack until they reach regions adjacent to the cathodes where the concentration of hydroxide ions is such that the solubility product of the particular metal hydroxide is exceeded. As the temperature of the system increases, the precipitates would tend to transform to hydrated metal oxides. Build-up of stress then occurs anew, until crack propagation is again 'triggered'. This process is autocatalytic, since it would continue, under constant conditions, until the crack had penetrated the entire metal section.'

The experimental data and micrographs cited in support of this theory were derived from studies on 18–8-type chromium-nickel austenitic stainless steels.

The presence of inert, hydrated oxide corrosion product in the crack system was demonstrated by bromine-methanol etching of the cracked specimen. The preliminary data presented indicate that the corrosion product is, in relation to the basis metal, enriched in chromium, and that its structure is primarily of cubic spinel type. Microscopical examination showed that the corrosion product grows in a fringe- or fan-shaped form (following the advance of the crack) and exhibits a surface topography thought to be a replication of the transgranular fracture surfaces.

To determine whether hydroxides precipitating under constraint can exert hydrostatic pressure, a chloride solution of 18–8 stainless steel was electrolyzed within a narrow crevice in a birefringent plastic block. Circularly polarized light was employed to examine the stress distribution within the plastic block at the crevice notch. Qualitative confirmation was obtained that measurable stress build-up can occur by the mechanism proposed.

The paper closes with sections in which the author, by way of emphasizing the value of electron-microscopical studies of stress-corrosion-cracked stainless-steel surfaces, reports work on fracture faces, stress-corrosion microcracks, and initiation of cracks from pits. Oxide replicas of stress-corrosion microcracks in belt-ground 18–8 stainless steel revealed that the cracks consist of elongated grooves or troughs in the metal, primarily, but not always, transverse to the grinding direction. Each groove is the result of localized chloride corrosion of the surface containing residual grinding (tensile) stresses. At the base of the groove is a very narrow crevice in which a 'corrosion-product fan' only a few hundred angstroms thick grows into the metal. At the site of formation the 'fan' fills the crevice and develops the additional lattice-strain energy which, it is postulated, triggers propagation of the crack. From the thickness dimension of the 'fans' it is concluded that the radius of curvature of the root of the crack is of the order of lattice dimensions. On this basis a high stress-concentration factor is postulated, possibly approaching 1000.

Relationship between Microtopology of the Corrosion Product and Stress-Corrosion Failure

E. A. GULBRANSEN and T. P. COPAN: 'Effect of Stress and Environment on the Microtopology of the Corrosion Product', pp. 155–80.

The work described was carried out on the assumption that the first step in stress-corrosion fracture is a highly localized (rather than a uniform) reaction of the metal with the environment, and that localized chemical attack of the metal results in corrosion products of unusual crystal habits, or in the formation of localized pits or trenches in the metal. (In the case of reactions with gases or vapours, the reaction products will accumulate at the site of the reaction.)

The authors' aim is (1) to illustrate the effect of environment and stress on the crystal habits of the corrosion products formed on iron, nickel, chromium, and 18–8 Type 304 stainless steel, and (2) to demonstrate that certain crystal habits of the corrosion product indicate metallurgical structures susceptible to stress-corrosion cracking.

Tests were carried out on disc, wire and tensile-test specimens fabricated from 'Armco' iron, 'Puron' iron, high-purity nickel and chromium, and 18–8 (Type 304) stainless steel. Holes were drilled in the disc and tensile specimens. To avoid the complications associated with reactions in liquid environments, and because thermodynamic analysis of gas-phase chemical reactions is simpler, the authors based their experiments on gaseous environments: (1) dry oxygen, (2) oxygen saturated with water vapour at 25°C., (3) oxygen saturated with water vapour in the region of 100°C., and (4) pure steam. The specimens were exposed to the environment, with and without tensile stress, at temperatures in

Unusual Crystal Growths in Oxides on Metals and Steels

(*See abstract on p. 120*)

Type of Growth	Specimen	Reaction Conditions
Whiskers		
Diameter 300-900Å, α Fe_2O_3, average length 100,000Å, maximum length 220,000Å, surface density 5×10^7-10^8 per cm.^{2}.	'Armco' iron; disc.	Dry O_2 at 0·1 atm., 120 hours, 500°C.
Diameter 200-500Å, α Fe_2O_3, average length 30,000Å, maximum length 100,000Å, surface density $2\text{-}3 \times 10^7$ per cm.^{2}.	'Puron' iron; disc.	Dry O_2 at 0·1 atm., 48 hours, 500°C.
Rounded Platelets		
~ 100 Å thick, 30,000Å high, 70,000Å long, Cr_2O_3. (Also whiskers: diameter 100-200Å, length 30,000Å)	Chromium; disc.	Dry O_2 at 0·1 atm., 120 hours, 500°C.
Blade-Shaped Platelets		
~ 100 Å thick, 3,000-5,000Å wide, 15,000-25,000Å high.	'Armco' iron; disc.	H_2O vapour at 1·0 atm., 72 hours, 400°C.
Angular Platelets		
~ 100Å thick, 60,000Å wide, 30,000Å high.	Type 304 stainless steel; 9-mil. wire	Wet O_2 at 1·0 atm., 24 hours, 500°C.
Spikes		
2,000Å thick, 70,000Å long, NiO. (Also whiskers: diameter 200-500Å, length 10,000Å, surface density 2×10^7 per cm.^{2})	Nickel; disc.	Dry O_2 at 0·1 atm., 120 hours, 500°C.

the range 300°–800°C. The oxide and corrosion films formed were studied by electron-microscopical and electron-diffraction techniques.

These studies revealed the occurrence of several unusual crystal habits, which were a function of the environment and stress conditions (*see* table above). Annealed metals formed thin whiskers of oxide when reacted with dry oxygen, while blade-shaped platelets were formed in water-vapour atmospheres. Internal and external stress accentuated the platelet type of crystal habit, and stress appeared to align the nucleation centres of reaction. Carbide, nitride and other precipitates also played a major rôle.

It is proposed that the unusual crystal habits in the corrosion product are caused by localized chemical reaction in the vapour phase. Deep pits and trenches of corrosion product form at these active sites of reaction by a process which the authors designate 'chemical cutting'. Reactions in the liquid phase also occur at the active sites, with or without the build-up of unusual crystal habits. Corrosion under the influence of stress can therefore lead to sub-microscopic cracks and ultimate failure of the metal.

Stress Corrosion of Single Crystals of Stainless Steel

H. W. PAXTON, R. E. REED and R. LEGGETT: 'Stress Corrosion of Single Crystals of Stainless Steel', pp. 181–90; disc., pp. 190–1.

Work on the stress corrosion of austenitic stainless steels has been carried out almost exclusively on polycrystalline specimens, and has consequently involved difficulties in identifying the plane of fracture, the normal stress on this plane and the nucleation site. In the experiments now described an attempt has been made to obviate these difficulties by using single crystals of stainless steels.

Specimens cut from a single crystal of 20–20 chromium-nickel austenitic steel were stressed in tension in boiling magnesium chloride. Care was taken to remove the specimens before any crack covered more than 10 per cent. of the cross section. The data derived from subsequent metallographic examination are included in the paper, supplemented by photomicrographs illustrating cracks, pits and slip systems.

The most surprising feature of the investigation is considered to be the reasonably short time (relative to that associated with polycrystalline material) in which cracking occurred. It is noted that a simple qualitative rationalization of some of the stress-corrosion characteristics of stainless steel is obtainable on the basis of stacking-fault energy.

Development and Path of Stress-Corrosion Cracks in Austenitic Stainless Steels

J. G. HINES and R. W. HUGILL: 'Metallographic and Crystallographic Examination of Stress-Corrosion Cracks in Austenitic Cr-Ni Steels', pp. 193–223; disc., pp. 223–6.

The comprehensive metallographic study reported by the authors was undertaken in the hope that the results would throw light on the mechanism involved in stress corrosion of stainless steels. The mode of development of stress-corrosion cracks is of considerable theoretical interest, and study of the form and arrangement of such cracks at various stages in their development comprised an important part

of the investigation. Since a single section through a three-dimensional crack system does not provide an overall picture, and might indeed be misleading, it was considered essential to build up three-dimensional pictures of crack systems: the technique used, which involved repeated sectioning, is fully described. A study was made also of the relationship between the paths of the cracks and the microstructural or crystallographic features of the steel.

The development of stress-corrosion cracks was investigated by metallographic examination of wire specimens of austenitic stainless steel which had been exposed, under axial tensile stress, to boiling 42 per cent. $MgCl_2$ solution. The crack systems so determined, and the successive stages in the development of a fine crack, are diagrammatically represented.

The second phase of the study, which involved investigation of service failures as well as of specimens broken in laboratory tests, was concerned with the paths taken by cracks in austenite, the influence of the presence of δ-ferrite in duplex steels, and the influence of plastically deforming specimens of fully austenitic steel prior to cracking.

On the basis of the results obtained, crack development is divided into two stages: the formation of fine cracks which spread sideways faster than they penetrate into the material; and the formation of larger, open cracks which are extensively branched and which form from fine cracks after the commencement of yielding ahead of the crack.

In austenite, changes in the direction of the crack occur both within a grain and at grain or twin boundaries. The distribution of angles between sections of a crack within a single grain is compared in the paper with the calculated distributions expected if the cracks were following members of a set of simple crystallographic planes: it is concluded that, in softened material, cracks do not follow a single simple plane for distances greater than about 1μ.

In duplex steels containing ferrite or martensite the cracks occasionally pass through ferrite grains or martensite plates, but, more commonly, the crack path lies entirely in the austenite matrix. There is evidence that the mechanism of cracking is not the same in the body-centred lattice as in austenite.

In specimens plastically deformed before commencement of cracking, branching of fine cracks was more common than in fully-softened specimens.

Although the results presented are insufficient to confirm any of the mechanisms proposed for crack propagation in austenitic stainless steels, the authors list certain features which the investigation indicates must be capable of explanation before a theory can be recognized as valid.

Influence of Temperature on Stress Corrosion of Stainless Steels in Chloride Waters

W. W. KIRK, F. H. BECK and M. G. FONTANA: 'Stress-Corrosion Cracking of Austenitic Stainless Steels in High-Temperature Chloride Waters', pp. 227–36; disc., pp. 237–43.

Previous experiments by STAEHLE, BECK and FONTANA (to determine 'the effect of the relative availability of chloride and oxygen and the applied stress on the morphology of stress-corrosion cracks in austenitic stainless steels') had indicated that Type 347 niobium-stabilized 18–8 stainless steel is susceptible, under vapour-condensation conditions, to stress-corrosion cracking at stresses as low as 2000 p.s.i. at a chloride concentration of 50 p.p.m. of NaCl (see abstract in *Nickel Bulletin*, 1959, vol. 32, No. 9–10, pp. 305–6). The work now reported was carried out to provide further information on the conditions (in particular, on temperature effects) necessary for occurrence of stress-corrosion cracking in austenitic stainless steels.

Tests were carried out both on Type 347 and Type 316 (18–12Mo) stainless-steel specimens, which, prior to testing, had been held at 2000°F. (1095°C.) for ½ hour and then furnace-cooled. Preliminary autoclave tests under vapour-condensation conditions revealed that a NaCl concentration of 875 p.p.m. induced severe cracking at 400°F. (205°C.) within a short period of time. A solution of this concentration was therefore employed as the corrosive in a series of tests conducted at temperatures which, rising in intervals of 25F°. (14C°.), covered the range 150°–400°F. (65°–205°C.). The specimens were subjected to stresses of 5000 and 10,000 p.s.i. (2·2 and 4·5 t.s.i.; 3·5 and 7 kg./mm.²), and time to cracking was determined as a function of temperature. The results obtained revealed no significant difference between the cracking characteristics of the two steels.

The development of stress-corrosion cracks was studied in supplementary tests which were conducted using an apparatus designed to permit continuous observation of the specimen surface during tests at elevated temperatures and pressures (and which enabled crack initiation and propagation to be recorded on ciné films). To induce cracking in a reasonably short time, the specimens were exposed to conditions involving intermittent wetting and drying.

The results of the investigation are considered to warrant the following conclusions:

'(1) Reduced temperatures increase the time necessary for the onset of cracking in Types 347 and 316 stainless steel. However, there appears to be no effect on the minimum stress necessary for cracking to occur under conditions of vapour condensation. No differences are noted in the cracking characteristics of these steels.

'(2) Lowering the initial pH of the corrosive medium apparently has no effect on the stress-corrosion-cracking behaviour of austenitic stainless steels in a NaCl environment.

'(3) Intermittent wetting and drying of the stainless steel specimens must be accomplished to effect any localized attack by solutions of low chloride concentration. The nature of the cracks produced under these conditions is comparable to cracking in water phase testing at higher chloride concentrations. Extensive corrosion usually occurs on all parts of the crack.

'(4) The arresting point of a crack which does not produce complete failure has very little correlation with the structure of the material, the applied stress, or the chloride concentration of the corrosive medium.

'(5) Stress-corrosion cracking of Types 347 and 316 stainless steel in a NaCl environment is always initiated at the site of a pit. The geometry of the pits determines to a large extent whether cracking will or will not occur.

'(6) Stress-corrosion cracks in austenitic stainless steels propagate in a series of short bursts. Corrosion of the newly formed surfaces begins immediately after each progression. The base of the crack becomes sufficiently sharp during this period to produce a high strain energy and thus maintain progression through the bulk metal. The rate of surface-crack propagation is approximately 4 mm./hour or less.'

Stress Corrosion of Austenitic Stainless Steel by Hot Salts

H. W. PICKERING: 'Stress Corrosion of Austenitic Stainless Steel by Hot Salts', pp. 244–6.

This short paper is included with the aim of amplifying the findings of Kirk *et al.* (*see previous abstract*) by presentation of data on the stress corrosion of low-carbon 18-8 stainless steel (Type 304L) by hot sodium chloride and other salts.

Constant-load tensile tests were performed (in the temperature range 200°–1400°F. (95°–760°C.) and at applied stresses ranging from zero to the yield stress) on specimens coated with a $\frac{1}{16}$-in. (1·5-mm.) layer of the relevant salt by alternate dipping in the saturated salt solution and drying. Continuous-weighing tests were run to determine rates of attack. The results of the investigation to date are summarized as follows:

'(1) Stress-corrosion specimens of Type 304L stainless steel coated with NaCl failed intergranularly in less than 60 hours when exposed to air atmospheres in the temperature range 1100°–1400°F. (595°–760°C.) at stresses ranging from 4500 to 8000 p.s.i. (2–3·5 t.s.i.; 3–5·5 kg./mm.^{2}). Preliminary tests indicate the corrosion attack to be much less at temperatures below 1000°F. (540°C.).

'(2) Very rapid attack occurs on Type 304L stainless-steel specimens exposed to temperatures above 1100°F. This attack is extensive on both stressed and unstressed specimens and is related to the presence of the salt coating and oxygen in the atmosphere. Salt-coated specimens tested in an argon atmosphere (traces of oxygen may have been present) were only very slightly attacked.

'(3) The corrosion attack occurring at the higher temperatures (1100°F. and above) is intergranular in nature. Although considerably less surface attack occurs at the lower temperatures, intergranular failure results in times comparable to those mentioned above.

'(4) The corrosion attack is a basic factor in the mechanism of crack propagation.

'(5) A linear rate of corrosion is indicated by preliminary weighting tests at 1300°F. (705°C.). This is further indicated by the porous, nonadherent, and flaky nature of the corrosion scale. In these first weighting tests, some deviation from linear rate was found to occur in the first hour. Sublimation of NaCl does occur at this temperature, but it is suspected to have little effect on the rate data due to the high rates of oxygen pick-up that occur.

'(6) Salt (NaCl) transfer, due to migration and/or diffusion, occurs in spot tests at 1300°F. (705°C.) on 304L stainless steel.* This was indicated by rapid attack and an equally thick corrosion scale over the entire spot-test sample, including the bottom surface, after 15 hours at test temperature. The original droplet of NaCl was always intact at the completion of the test unless complete exhaustion of the NaCl occurred.

'(7) Sublimation studies at 1300°F. (705°C.) indicate rapid, overall attack. This attack, however, is not as severe as that which occurs on corrosion 'spot-test' samples tested for comparable times. Intergranular penetration was found to occur in both the spot tests and the sublimation studies.

'(8) NaF and NaBr cause rapid attack of 304L stainless steel at 1300°F. Salt transfer also occurred in spot tests at this temperature.'

Influence of Nickel Content on Stress Corrosion of Alloys and Steels

H. R. COPSON: 'Effect of Composition on Stress-Corrosion Cracking of Some Alloys Containing Nickel', pp. 247–67; disc., pp. 267–9.

In the introductory section of the paper the author reviews the literature relating nickel content to the resistance of stainless steels to stress corrosion, and concludes that none of the mechanisms proposed in explanation of such attack satisfactorily account for the beneficial effects of high nickel content. The work described originated in this conclusion, and was carried out with the aim of determining the relationship between high nickel content and susceptibility to cracking, and hence of throwing light on the mechanism involved.

Three systems were studied: the iron-nickel-chromium, the iron-nickel and the nickel-copper. The scope and salient findings of the investigation are outlined below.

Iron-Chromium-Nickel Alloys

The main phase of the test programme was concerned with determination of the time-to-cracking of wire specimens (drawn down from 26 laboratory-melted alloys) which were loaded in tension during exposure to boiling 42 per cent. magnesium-chloride solution. The nickel content ranged from 8 to 77 per cent., and, in general, the chromium content was in the range 18–20 per cent. Some of the alloys contained small amounts of niobium, titanium, or molybdenum, and two contained molybdenum, copper and niobium

* The tests were run to study the effect of salt concentrated on a small area of an otherwise uncoated specimen.

(or titanium) additions. Carbon, nitrogen, silicon and manganese contents were intended to be within the usual commercial ranges. The wires were finished in three different tempers: annealed, partially-hardened and fully-hardened. Three lots of commercial chromium-nickel stainless-steel wire were included in the tests: Types 304, 316 and 310 (18-8, 18-13Mo and 25-20).

Some specimens containing 8 per cent. nickel failed within an hour, whereas with those of high nickel content (i.e., greater than 45-50 per cent.) no signs of cracking were evident at the end of the 3-day tests. A curve representing the minimum time-to-cracking as a function of nickel content, and enclosing all the cracking failures, is of U-shape, one arm extending to zero nickel content (the literature indicates that as the concentration of nickel increases from zero the time to cracking decreases to a minimum in the region of 6-8 per cent.), the other extending to the region of 45-50 per cent. of nickel, where immunity is attained. Attention is drawn to the striking similarity of this curve to those drawn by GRAF for homogeneous alloy systems ('Stress-Corrosion Cracking and Embrittlement', published by Wiley, New York, 1956). If it is assumed that GRAF's rules apply in this case, however, nickel would have to be the more noble constituent: particulars of experiments carried out to investigate the validity of such an assumption are given by the author.

The presence of small amounts of titanium, niobium, molybdenum or copper, and variations in the chromium content, appeared to be without significant effect.

Iron-Nickel Alloys

(1) Nickel, a carbon steel, and iron-base alloys ranging in nickel content from 2·02 to 37·75 per cent. were exposed, in the form of U-bend specimens, to boiling 33 per cent. sodium-hydroxide solution containing 0·13 per cent. lead oxide and 0·13 per cent. sodium chloride.

The findings after 14 days indicate that the susceptibility of steel to cracking in sodium-hydroxide solutions increases with increase in nickel up to a content of at least 8·5 per cent. Somewhere in the range 8·5-38 per cent. nickel the iron-nickel alloys acquired increased resistance to cracking. With the exception of cracking in the carbon steel (0 per cent. nickel), the effects of nickel content were similar to those determined in the tests on austenitic stainless steels. (It is noted, however, that steels are known to be susceptible to stress-corrosion cracking in caustic solutions, and that factors other than nickel content are involved.)

(2) U-bend specimens of nickel, carbon steel, and iron-nickel alloys ranging in nickel content from 2·02 to 41·79 per cent., were exposed to boiling 42 per cent. magnesium-chloride solution. The findings were similar to those established in the other tests. Susceptibility to cracking increased with nickel content up to the region of 9 per cent.; a trend which was reversed with larger amounts of nickel (alloys of high nickel content appeared to be immune to cracking). Whether the structure of the material was austenitic or ferritic appeared to make little difference to the results obtained.

Nickel-Copper Alloys

U-bend specimens of nickel, and of nickel-copper alloys containing 66, 31, 30 and 15 per cent. of copper, were exposed to the vapour present above 48 per cent. hydrofluoric acid and to that present above 30 per cent. hydrofluosilicic acid. The alloys with 15 and 30 per cent. copper suffered severe stress-corrosion cracking, but that containing 66 per cent. copper was resistant to cracking in tests lasting 14 days. The corrosion behaviour of nickel could not be determined with certainty, but age-hardened specimens of 'Duranickel' cracked rapidly under the test conditions. The results are considered to indicate that susceptibility to cracking varies with the nickel/copper ratio in a manner in agreement with the Graf theory.

In other experiments U-bend specimens of 18-8 chromium-manganese stainless steels containing 0·13 per cent. nickel and 0·08 per cent. copper were exposed to boiling 42 per cent. magnesium-chloride solution. Hot-rolled material showed no signs of cracking in tests lasting 21 days. A cold-rolled-and-annealed strip specimen cracked in less than one day.

The implications of the results are briefly discussed.

Effect of Neutron Irradiation on Susceptibility of Austenitic Stainless Steel to Stress Corrosion

C. R. CUPP: 'Effect of Neutron Irradiation on Post-Irradiation Stress-Corrosion Cracking of Stainless Steel', pp. 270-2.

Three groups of Type 304 18-8 stainless-steel wire were exposed to neutron irradiation and, after several months' storage, were subjected to stress-corrosion tests in boiling 42 per cent. magnesium-chloride solution. Un-irradiated Type 308 stainless-steel specimens were also tested.

The average time-to-fracture of the irradiated specimens (71 minutes) was approximately the same as that for steels of Type 304 (79 minutes) and Type 308 (72 minutes) in the un-irradiated condition. It is concluded that the irradiation had no influence on the susceptibility of stainless steel to post-irradiation stress-corrosion cracking.

Influence of Age Hardening on the Susceptibility of a Copper-Nickel-Silicon Alloy to Stress Corrosion

W. D. ROBERTSON, E. G. GRENIER, W. H. DAVENPORT and V. F. NOLE: 'The Dependence of Stress-Corrosion-Cracking Susceptibility on Age Hardening in a Copper-Nickel-Silicon Alloy', pp. 273-89; disc., pp. 289-92.

The investigation reported was undertaken to study, at each stage in the hardening process, the stress-corrosion characteristics of the copper-nickel-silicon age-hardenable alloy 'Silnic', and, in particular, (1) to determine whether the time and temperature of heat-treatment producing optimum mechanical

properties would influence susceptibility to failure in a corrosive environment, and (2) to investigate the influence of structure on stress-corrosion cracking of a copper-base alloy in which the structure was varied by heat-treatment and deformation.

The specimens tested contained 1·73–1·93 per cent. nickel and 0·51–0·73 per cent. silicon. The stress-corrosion characteristics of the alloy in the various conditions studied were evaluated by exposing specimens, under load, to an atmosphere consisting of air 80, ammonia 16, water vapour 4, per cent., fed through a test chamber maintained at 35°C. A study was made of the influence, on susceptibility to stress-corrosion cracking, of the following factors: deformation prior to ageing; time and temperature of ageing; cold working in the absence of ageing; deformation prior and subsequent to ageing.

The data presented, which are supplemented by numerous photomicrographs exemplifying the types of corrosive attack determined, establish that susceptibility to stress-corrosion cracking in ammonia was dependent on ageing time and on the extent of plastic deformation preceding or following ageing. The maximum stress which the alloy can sustain for 1,000 hours without failure increased rapidly with increase in the extent of deformation prior to ageing; moreover, the relative loss in strength at the endurance limit diminished as the strength was increased by cold working, indicating an absolute decrease in susceptibility to cracking. Deformation of the alloy subsequent to ageing also diminished susceptibility, though to a lesser degree than deformation prior to ageing.

In the absence of deformation, the corrosion path followed the grain boundaries, and, occasionally, coherent twin boundaries. Transgranular structural paths, which appeared to be deformation bands, became preferential paths of corrosion in the plastically deformed alloys, but the rate of penetration of the alloy section seemed to diminish with increase in the number of sites of preferential corrosion produced by deformation.

Corrosion of Ancient Bronze

C. S. SMITH: 'Corrosion of an Ancient Bronze and an Ancient Silver Alloy', pp. 293–4.

Report of microstructural studies of 12th century silver-copper-alloy sheet and of Greek bronze sheet (the latter having lain immersed in the Mediterranean Sea for over 2,000 years).

Stress-Corrosion Cracking of Low-Carbon Steel

H. L. LOGAN: 'Stress-Corrosion Cracking in Low-Carbon Steel', pp. 295–309; disc., pp. 309–10.

The results are presented of a study of stress-corrosion cracking of low-carbon-steel specimens, some of which had been decarburized and heat-treated to produce surface crystals sufficiently large to permit determination of their orientations. A film-rupture mechanism of crack propagation is postulated.

Cracking of Steel under Stress in the Presence of Hydrogen

P. G. BASTIEN: 'The Phenomena of Cracking and Fracture of Steel in the Presence of Hydrogen. Corrosion under Stress in the Presence of Moist Hydrogen Sulfide', pp. 311–38; disc., pp. 339–40.

The paper comprises a report of the comprehensive work carried out (1) at the Metal Physics Research Centre of the Ecole Centrale, Paris, on the embrittlement of steels by hydrogen and, in particular, on the cracking encountered in tubing steels exposed under stress to moist hydrogen-sulphide gas in the Lacq oil field, and (2) at the Schneider Works on the development of steels resistant to such failure.

It is shown that the susceptibility of a steel to hydrogen embrittlement is largely dependent on its microstructure, and that plastic deformation is necessary if the effects of embrittlement are to appear. A mechanism is proposed in explanation of the embrittlement of iron and steel by hydrogen.

Stress-Corrosion Cracking of Mild Steel

H. J. ENGELL and A. BÄUMEL: 'The Electrochemical Mechanism of Stress-Corrosion Cracking of Mild Steel', pp. 341–63; disc., pp. 363–72.

The study of the electrochemistry of the iron/nitrate-solution system described in the paper is presented as a contribution to work on the stress corrosion of mild steel. An attempt is made to throw light on (1) the chemical and electrochemical properties of the solution necessary for stress corrosion, and (2) the electrochemical reactions occurring during stress corrosion of mild steel in concentrated calcium-nitrate solutions.

Current Approaches to the Problem of Stress Corrosion

L. R. SCHARFSTEIN: 'Current Problems for Additional Consideration', pp. 373–9.

In this concluding paper of the Conference the author comments on those aspects of the subject which seem of importance for future consideration. In this connexion he discusses the following points: mechanism for the initiation of cracking; theories of crack propagation; wedging effect; three-dimensional factors in crack growth; hydrogen embrittlement and proton mobility; and the influence of composition and of plastic deformation on susceptibility to cracking.

(*End of Symposium*)

Anodic-Passivation Studies of Stainless Steels

J. D. SUDBURY, O. L. RIGGS and D. A. SHOCK: 'Anodic Passivation Studies.'

Corrosion, 1960, vol. 16, Feb., pp. 47t–54t; disc., p. 54t.

To render a steel passive in a specific environment, it is necessary only to maintain its potential within the passive range delimited by the relevant polarization curves. Much work has been carried out to determine the feasibility of applying this technique

Current Density Required to Maintain Passivity of Various Metals in 67 per cent. H_2SO_4

(*See abstract on p. 125*)

Material	Current Density, Micro-amps per cm.²	Potential Between Anode and Cathode, mv.	Total Film Resistance, Ohms per cm.²
Type 302 Steel	2·2	−1,100	500,000
„ 304 „	3·8	−850	224,000
„ 310 „	0·5	−1,050	2,100,000
Type 316 Steel	0·1	−1,750	17,500,000
„ 405 „	2·7	−900	333,330
„ 410 „	10·9	−1,100	100,900
Type 446 Steel	0·7	−1,250	1,786,000
Mild Steel	15·0	−380	26,000
Titanium	0·08	−1,400	17,500,000
'Hastelloy B'	0·5	90	180,000
'Carpenter 20'	0·03	−1,400	46,000,000

to protection of industrial plant, but developments have been hindered by the difficulty of maintaining the desired potential in the case of the very large currents required for industrial applications. The anodic-polarization studies summarized in the present paper were conducted to obtain information which would allow definition of systems in which anodic protection is theoretically possible.

After a brief review of the theories advanced in explanation of the mechanism of passivity, the authors describe the corrosion-test system and the passivation procedures employed in the investigation. The potentiostat used in the experimental work was similar to that previously used by HICKLING (*Trans. Faraday Soc.*, 1942, vol. 38, p. 27). Most of the results presented were obtained using 67 per cent. sulphuric acid.

The following factors were studied: potential shift during passivation, current-density requirements, and the influence of surface preparation, sulphuric-acid concentration, surface area, temperature, specimen composition, the chemical environment, agitation and the 'throwing power' of the electrochemical cell. The properties of the film formed during passivation were investigated by electron microscopy, and account was also taken of the possibility of the occurrence of cracking in stainless steel as a result of anodic polarization.

Steels and alloys successfully passivated include those for which data are reproduced in the table above.* Apparently all the ferrous materials can be successfully passivated, but not those of copper-base. *Data for other environments are presented in the paper referred to in the following abstract.*

The conventional potentiostat was used for most of the laboratory work. Where surface areas larger than a few square centimetres are involved, this device was not, however, capable of supplying adequate current to maintain the passivity of the metal, and it was necessary, in order to render the passivation technique applicable to large-scale processes and storage vessels, to evolve a potential controller capable of supplying very large currents (up to several hundred amperes). The authors' work has led to the development of an anodic-protection system which is claimed to control corrosion in large vessels. The main purpose of this paper is not to describe the system in detail, but to report the results which are obtainable by its use. *The papers referred to in the following two abstracts emphasize the type of application for which the system is suitable.*

Attention is drawn to pilot studies in which corrosion of a 500-gallon 18-8 Type 304 stainless-steel tank filled with 67 per cent. H_2SO_4 was eliminated for indefinite periods by application of negligible currents.

See also

Application of Anodic Protection in the Chemical Industry

D. A. SHOCK, O. L. RIGGS and J. D. SUDBURY: 'Application of Anodic Protection in the Chemical Industry.' *Corrosion*, 1960, vol. 16, Feb., pp. 55t-8t; disc., p. 58t.

In this paper, which is complementary to those to which attention is directed in the preceding and following abstracts, the authors discuss the factors to be taken into account in evaluating the feasibility of applying anodic protection to a specific metal/electrolyte system: i.e., initial current requirements, limitations with respect to the passivity range, current requirements to maintain passivity.

The method cited as the general means of investigating the feasibility of using anodic passivation involves anodically polarizing the proposed metal in the corrosive environment within the temperature range in which the vessel will operate in service. From the data obtained and the surface area to be protected, the total current necessary to produce and maintain passivation can be determined. If the initial passivating current required is of the order of several hundred amps., and if the passive range is not less than 50 millivolts and can be maintained with a small minimum current, the system can be installed to make and maintain a passive surface. The cost will depend on the current required to maintain passivity and on the capital cost associated with the size and complexity of the controller equipment.

Anodic polarization is shown to be applicable

* In answering questions put during the discussion, the authors comment that their investigations indicate that pure nickel and high-nickel alloys are not rendered passive by anodic polarization. Erratic, unstable potentials have been associated with all the work carried out on polarization of nickel.

Current-Density Requirements for Type 304 Stainless Steel in Different Chemical Environments

(*See abstract on p. 126*)

System	Current Density (μ amp./in.^{2})	
	To Obtain Passivity	To Maintain Passivity
LiOH (pH of 9·5)	516	0·14
NaOH (20% Caustic)	30,000	64
H_2O_2	64	1·3
NH_4NO_3	580	5·1
$Al_2(SO_4)_3$	580	5·2
H_2SO_4 67%		
75°F. 25°C.	3,300	0·6
180°F 82°C.	30	1·9
H_3PO_4 115%		
75°F. 25°C.	0·1	0·001
180°F. 82°C.	0·2	0·001
350°F. 175°C.	416	14·0
HNO_3 80%		
75°F. 25°C.	16	0·2
180°F. 82°C.	75	0·7

to numerous oxidizing environments with the necessary conductivity. In general, the oxy acids, the bases and the salts fall within the scope of the technique. It has, however, been found impossible to establish passivity in reducing systems such as HCl, NaCl, $FeCl_2$, $SnCl_2$, $HI.H_2O$, although certain amounts of these substances can be tolerated in oxidizing systems.

The table reproduced above summarizes current-density requirements for Type 304 18-8 chromium-nickel stainless steel in a number of systems discussed by the authors as amenable to anodic protection.

See also

Anodic Protection of Stainless-Steel Equipment in a Sulphonation Plant

O. L. RIGGS, M. HUTCHISON and N. L. CONGER: 'Anodic Control of Corrosion in a Sulfonation Plant.'
Corrosion, 1960, vol. 16, Feb., pp. 58t–62t.

Laboratory studies having indicated that anodic protection could be used to advantage in protecting units in a sulphonation plant, it was necessary, since the available electrodes were not suited to systems involving high temperatures and extreme agitation, to design platinum electrodes and reliable reference electrodes. The results of basic research led to the development of a new high-current automatic potential controller designed to fulfill the predicted current demands for anodic protection of plant used in the caustic neutralization of sulphonic acids: in particular, the apparatus was designed to confer anodic protection on an 18-8 Type 304 stainless-steel sulphonic-acid-neutralization vessel and the attendant mild-steel oleum-storage tank. In this paper details are given of the preliminary laboratory studies, the installation of the potential controllers, and the degree of protection obtained (the equipment has been in use for a year).

The efficacy of automatic anodic protection is assessed in terms of (1) the reduction in iron concentration throughout the process; (2) improvements in the quality of the product due to the absence of coloured iron salts; (3) increases in the productivity of the plant due to more rapid product/hydrocarbon separation as a result of the absence of iron soaps.

Potentiostatic Isolation of Microstructural Phases in Nickel Alloys

C. ILSCHNER-GENSCH: 'Potentiostatic Isolation of Microstructural Constituents in Nickel Alloys.'
Archiv f. d. Eisenhüttenwesen, 1960, vol. 31, Feb., pp. 97–102; disc., p. 102.

The application of electrolytic-isolation techniques to nickel-base materials is rendered difficult by the particular electrochemical characteristics of such alloys: the passivity of the matrix and the fact that the electrochemical potentials of the phases present differ only slightly. It is essential therefore to ensure that the potential difference between the specimen surface and the solution is maintained during the isolation reaction exactly at the appropriate value (details are given of the potentiostat used for this purpose in the present study). The potential values suitable for dissolution and isolation of a specific phase can be determined by evaluation of the current-density/potential curves established by tests on macroscopic specimens of the phases presumed to be present in the microstructure. This approach

to the problem was adopted by the author in the work now reported.

Current-density/potential curves were determined, in various electrolytes, for nickel, chromium, a 75-25 nickel-chromium alloy, and synthetically-produced specimens of the following secondary phases associated with nickel-chromium-base alloys: Ni_3Al, Ni_3Ti, Cr_7C_3 and $Cr_{23}C_6$. The curves obtained (which are presented and discussed) then provided a means of delimiting the potential regions in which phase separation appeared promising.

In much of the paper the author is concerned with the experiments which were conducted, using an electronic potentiostat, in an attempt to isolate the phases present in an alloy of the following composition: nickel 73·9, chromium 20·2, aluminium 1·9, titanium 1·9, iron 1·9, carbon 0·02, silicon 0·07, per cent. Specimens were studied in four conditions of heat-treatment: 8 hours at 1080°C.+16 hours at 700°C.; or 8 hours at 1080°C.+ 16 hours at 700°C.+ 100 or 500 or 1000 hours at 750°C. The data presented reveal that in a 10 per cent. phosphoric-acid electrolyte the γ' phase and the carbides were isolated from the matrix at an anode potential of +975 mV. In an electrolyte containing potassium bromide 1, sodium citrate 5, citric acid 5, per cent., dissolution of both the γ' phase and the matrix was achieved at a potential of +500 mV.

The isolated residues were subjected to micro-chemical, X-ray and electron-microscopical examination (photomicrographs illustrating the electron-microscopical study are included in the paper). Potentiostatic etching enabled comparison of γ' phase *in situ* and after isolation.

Corrosion-Resistance and Weldability of Chromium-Manganese-Nickel Austenitic Stainless Steels

D. WARREN: 'Corrosion and Weldability Studies on Chromium-Manganese Austenitic Stainless Steels.' *Corrosion*, 1960, vol. 16, Mar., pp. 119t-30t.

The investigation described was initiated to evaluate the corrosion-resistance and weldability of four austenitic stainless steels representative of the lean-nickel grades, i.e., one steel of 17-15 chromium-manganese-nitrogen type and the following three of chromium-manganese-nickel type: 'T.R.C.' (15-17-1), A.I.S.I. Type 201 (17-6-4) and A.I.S.I. Types 202 and 202L (18-8-5). Type 430 (17 per cent. chromium) and Type 304L (low-carbon 18-8 chromium-nickel) stainless steels were included in the test programme as standards of comparison.

Corrosion-resistance was determined in relation to more than twenty different environments, classifiable as follows: (*a*) mildly to moderately corrosive (cold organic acids, hot and cold nitric-acid solutions, and environments which produce rusting or product contamination); (*b*) more severely corrosive (i.e., those environments in which Type 304 stainless steel corrodes at a rate of 1-2 mils/month or displays borderline passivity); (*c*) those selected as a basis for pitting tests; and (*d*) boiling 65 per cent. nitric acid (resistance to which was employed as a criterion of susceptibility to intergranular corrosion following heat-treatment).

Only the Type 202, the chromium-manganese-nitrogen and the Type 304L stainless steels were included in the phase of the investigation concerned with assessment of welding characteristics. All three materials were evaluated in relation to the use of metallic-arc and tungsten inert-arc processes. This evaluation involved radiographic examination, guided bend tests and tensile tests.

The data obtained, which are presented *in extenso*, lead the authors to conclusions which they summarize as follows:

'*Mildly-to-Moderately-Corrosive Environments.* The corrosion-resistance of Type 202 was equivalent to that of Type 304 in all environments of this type. These environments included all types of cold organic acids, strongly oxidizing acids at temperatures up to 60°C., and environments which produced rusting. Corrosion-resistance of Cr-Mn-N stainless steel in these environments was good, but in some cases it was not equivalent to that of Type 202. 'TRC' steel was inferior to the other lean-nickel steels because of its lower chromium content.

'*More-Severely-Corrosive Environments.* In non-oxidizing environments of a severely corrosive nature, corrosion-resistance of Type 202 was equal to that of Type 304. In some cases it was even superior.

In strongly oxidizing environments, such as boiling 30 per cent. and 65 per cent. nitric acid, corrosion-resistance of Type 202 was inferior to that of Type 304, but was still within the useful range (corrosion rates of 0·0015 in./month or less).

'*Intergranularly-Corrosive Environments.* The intergranular corrosion resistance of Type 202L (0·03 per cent. maximum C) was comparable to that of Type 304L (0·03 per cent. maximum C) when both steels were heat-treated for 1 hour at 1250°F. (675°C.), water quench.

'*Weldability and Strength.* Weldability of Cr-Mn-N and Type 202 stainless steels was good, and was comparable to that of Type 304. Tensile strengths of butt-welded joints of the lean-nickel steels were appreciably higher than those of Type 304.'

Corrosion Tests on a Sintered Nickel-Iron-Molybdenum Alloy

H. J. BOOSS: 'Corrosion Tests on a Sintered Alloy with 60% Ni, 20% Fe and 20%Mo.'

Archiv f. d. Eisenhüttenwesen, 1960, vol. 31, Mar., pp. 195-7.

Among the materials used in the radio industry for grids and other component parts of valves is a 60-20-20 nickel-iron-molybdenum alloy produced by powder-metallurgical techniques and delivered in the form of wire and sheet. In contrast to its melted equivalent ('Hastelloy A'), this sintered alloy has been the subject of few corrosion studies, and, since the material is frequently subjected to electrochemical surface treatment, the author deemed it useful to

determine its corrosion behaviour in aqueous solutions. The data obtained from the investigation carried out in this connexion are summarized in the present paper.

The loss-in-weight of cold-rolled sheet specimens 0·2 mm. thick was determined, at 21°C., as a function of immersion time in, and concentration of, the following acids: nitric acid, sulphuric acid, hydrochloric acid, citric acid, acetic acid, tartaric acid, fluoric acid and phosphoric acid.

The specimens were found to be very resistant to corrosion by concentrated acid, but when exposed to solutions of lower concentration they were severely attacked (particularly at the longer test durations).

The specimens were severely attacked also in cyclic corrosion tests, which involved cyclic exposure to air of varying moisture content (and, in some cases, with sulphur-dioxide and carbon-dioxide additions), exposure to salt-water spray, or periodic immersion in distilled water.

In other tests the tensile strength and elongation at fracture of wire (cold drawn to 0·05-mm. diameter and then annealed at 1200°C. in hydrogen) was determined as a function of the wire's exposure to sulphuric acid, citric acid or tartaric acid. The deleterious effects of such exposure were found to be greater than would be commensurate with the effects of the decrease in cross section associated with corrosion.

Heat-Treatment of Stainless Steels

C. W. SHERMAN: 'The Right Heat-Treatment Keeps it Stainless.'

American Machinist, 1959, vol. 103, Sept. 7, pp. 132–6.

The various grades of stainless steel differ in their response to heat-treatment: some (the martensitic and precipitation-hardenable grades) can be hardened and tempered; others (the austenitic and ferritic) cannot. Where, moreover, the austenitic stainless steels are used in applications requiring corrosion-resistance, special precautions are necessary to prevent, or eliminate, carbide precipitation due to exposure to temperatures in the sensitization range. In this article the author outlines the types of heat-treatment relevant to the four grades of stainless steel, and indicates the circumstances under which each treatment is applicable.

Notes and tabular data on the heat-treatment of martensitic stainless steels (process-annealing, full-annealing, hardening, stress-relief and tempering treatment) are followed by a section concerned with the austenitic stainless steels (stress-relief treatment and the avoidance of deleterious carbide precipitation). Solution-annealing treatments are recommended for the various grades of A.I.S.I. 300 series of chromium-nickel austenitic stainless steels, and the annealing of the ferritic grades is also discussed. Heat-treatment of the precipitation-hardening grades is typified in relation to the procedures applied to '17-4 P.H.', '17-7 P.H.' and 'P.H. 15-7 Mo'.

In the brief penultimate section of the article the author comments upon the effects, deleterious and beneficial, of fabrication techniques which involve exposure to heat, and in the final section he outlines the equipment used in, and summarizes the precautions to be taken prior to, heat-treatment of stainless steels.

Consumable-Electrode-Melted Corrosion- and Heat-Resistant Steel

SOC. AUTOMOTIVE ENGINEERS: 'Steel Corrosion- and Heat-Resistant, 15Cr-26Ni-1·3Mo-2·1Ti-0·3V, Consumable-Electrode-Melted, Annealed (1650F.).' *Aeronautical Materials Specification* 5734, issued Jan. 15, 1960.

Covers, bars, forgings, mechanical tubing, forging stock and heading stock intended for use primarily in applications requiring high-strength up to 1300°F. (705°C.) and oxidation-resistance up to 1500°F. (815°C.) (e.g., in parts such as turbine rotors, shafts, buckets or blades, vanes, dowels, flanges and fittings).

Requirements are laid down with respect to condition, heat-treatment, mechanical (including stress-rupture) properties, hardness, grain-size, quality, dimensional tolerances, etc. Compositional requirements are as follows: carbon 0·08 max., silicon 0·4–1, manganese 1–2, phosphorus 0·04 max., sulphur 0·03 max., nickel 24–27, chromium 13·5–16, molybdenum 1–1·5, titanium 1·9–2·35, boron 0·003–0·01, vanadium 0·1–0·5, aluminium 0·35 max., per cent.

ANALYSIS

Check-Analysis Limits for Wrought Low-Alloy Steels

See abstract on p. 112.

Corrigendum

Chemical Deposition of Nickel-Boron and Cobalt-Boron Alloys

Nickel Bulletin, 1960, vol. 33, No. 1–2, p. 34.

In the reference to the patent abstracted under the above heading,

for *French Pat.* 1,977,797

read *French Pat.* 1,197,797.

Attention is drawn to the fact that many of the names of materials mentioned in The Nickel Bulletin are *Registered Trade Marks*.

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